PostDoc Journal
Vol. 4, No. 5, May 2016

Journal of Postdoctoral Research
www.postdocjournal.com

Boc-Pyranones as building block towards biologically important Oligosaccharide Natural Products

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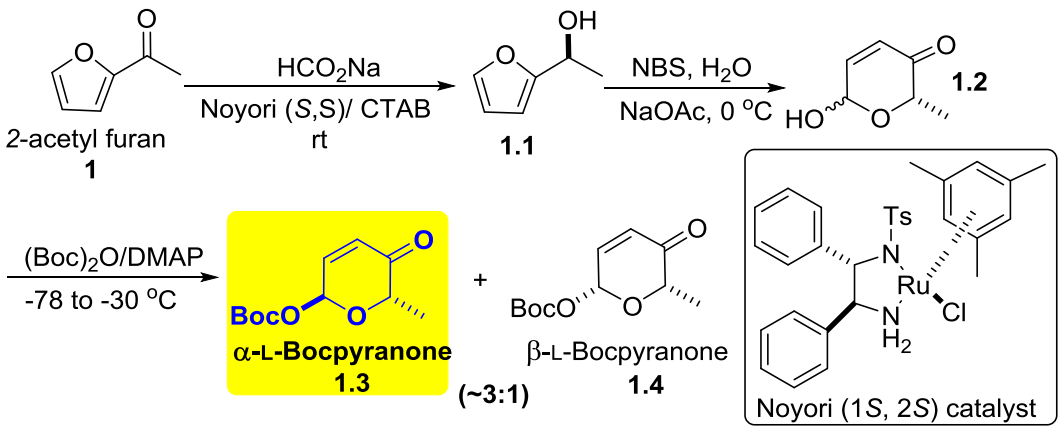
Abstract:

Pyranones play an important role towards the synthesis of carbohydrate containing natural products and are the key building blocks for most of the natural/unnatural oligosaccharides. Boc-Pyranones synthesis is a *De Novo* approach (*i.e*, achiral starting material, 2-acetyl furan (**1**) converted to chiral products) via Noyori asymmetric hydrogenation, Achmatowicz oxidative rearrangement, Upjohn dihydroxylation. Particularly, Boc-protected pyranones have established broad applications towards the synthesis of natural/unnatural products containing carbohydrate motifs (*e.g.,* total synthesis of mezzettiasides, a class of partially acetylated anti-cancer natural products via Pd-/B-dual catalysis and synthesis of cleistriosides/cleistetrosides, a series of *rhamno*-oligosaccharides).

Keywords: Boc-Pyranones, mezzettiasides, cleistrio-/cleistetro-sides, regioselective Pd-/B- glycosylation.

De Novo approach towards Boc-Pyranones:

Carbohydrates not only act as an energy storage but also play vital role in various biological processes (viral infection/tumor cell metastasis, immune response).[1-4] In particular, Boc-protected pyranones act an precursor or building blocks towards the synthesis of variety of the natural/unnatural products containing carbohydrate motifs (*e.g.,* mezzettiasides, Cleistriosides/Cleistetrosides).[5-8] The unique feature of this methodology is the conversion of achiral 2-acetyl furan (**1**) to chiral products using asymmetric catalysis and the concept is termed as *De Novo* approach to carbohydrates. This *de novo* approach installs the desired functionality and chirality in the sugar from achiral framework.[14-21] This method of synthesizing oligosaccharides is exceptional as compared to classical methods where carbohydrate containing building blocks are used as starting material by utilizing protection/deprotection strategies, thus increases the reaction sequence. Boc-Pyranones synthesis is very robust, highly scalable and starts from 2-acetyl furan (**1**) (commercially available and inexpensive). 2-acetyl furan upon treatment with Noyori (*S,S*) catalyst in presence of HCOONa (hydrogen source) provided the corresponding furan alcohol (**1.1**) with '*S*' configuration. Alcohol (**1.1**) further underwent Achmatowicz oxidative rearrangement ($NBS/NaOAc/H_2O$)[5-7,17-24] to provide an inseparable mixture of hemiacetal (**1.2**) followed by hydroxyl protection using $(Boc)_2O$/DMAP at -78 ^oC to provide the corresponding α-L-Boc-Pyranone (**1.3**) and β-L-Boc-Pyranone (**1.4**) in ~3:1 ratio (55-60% over 3 steps, Scheme 1). The Boc-protected pyranones act as a glycosyl donor under typical Pd-catalyzed glycosylation reaction conditions and reacts readily with glycosyl acceptor in various solvents (*e.g.*, CH_2Cl_2, THF).

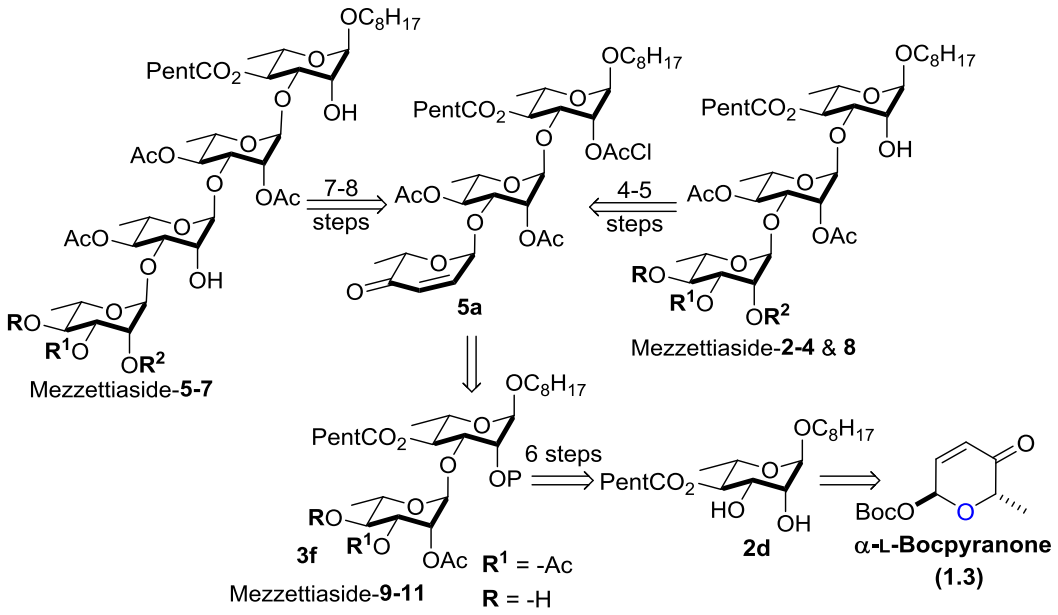


Scheme 1: *De Novo* approach towards Boc-Pyranones using acetyl furan

In conclusion, using a 3 step sequence, the achiral starting material 2-acetyl Furan (**1**) was converted to any possible stereoisomers of the Boc-Pyranones (**1.3/1.4**). The synthesized α-L-Boc-Pyranone (**1.3**) has wide range of applications towards natural/unnatural products containing carbohydrate skeleton (*e.g.*, mezzettiasides & cleistrio-/cleistetro-sides) as outlined below.

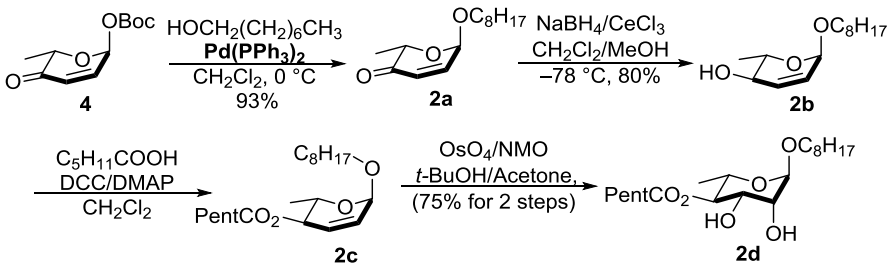
Application of α-L-Boc-Pyranone in the total synthesis of Mezzettiaside natural products via Pd-/B-dual catalysis:

Mezzettiasides, a class of anti-cancer natural products were isolated from the stem and fruit bark of *Mezzettia leptopoda* from Malaysian island of Borneo by kinghorn *etal* and waterman *etal* respectively. [1-4] The important feature which makes these class interesting for synthesis is its unique partially acylated oligorhamnoside structure and rare 1,3-linked carbohydrate motifs which can be constructed utilizing α-L-Boc-Pyranone **1.3**. These anti-cancer natural products are divided into three subclasses: disaccharide (mezzettiasides-**9**-**11**), trisaccharide (mezzettiasides-**2**-**4**&**8**) and tetrasaccharide (mezzettiasides-**5**-**7**). The synthesis of all the 10 natural products was achieved using a divergent approach, thus allowing minimal use of protecting group in combination with Pd-/B-dual catalysis to accomplish the desired regio- and stereo-selectivity. This approach makes use of masked enone as an atom-less protecting group and only one protection (-AcCl) was used throughout the synthesis of mezzettiasides.[3] Retrosynthetically, both tetrasaccharides (mezzettiaside-**5**-**7**) and trisaccharides (mezzettiaside-**2**-**4**&**8**) could be obtained from a common trisaccharide enone precursor (**5a**). The trisaccharide intermediate **5a** was obtained from protected disaccharide intermediate (**3f**) under Pd-catalyzed glycosylation with Boc-Pyranone (**1.3**). Whereas, the intermediate disaccharide **3f** was synthesized in 6 steps from monosaccharide diol **2d** having a C-4 hexanoate side chain. Whereas, the synthesis of diol **2d** was accomplished using α-L-Boc-Pyranone **1.3** in just 4 steps (Scheme 2).



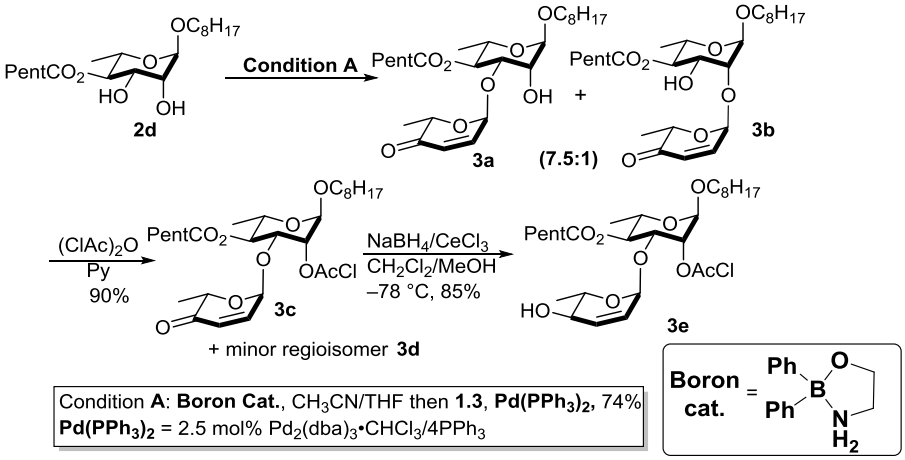
Scheme 2: Retrosynthetic analysis of Mezzettiasides

These divergent synthesis of all the 10 natural products started with Boc-Pyranone **1.3** which was prepared in 3 steps from acetyl furan **1** (Scheme 1). In this regard, Boc-Pyranone **1.3** upon glycosylation with 1-octanol using $Pd_2(dba)_3{\cdot}CHCl_3/4PPh_3$[16] provided the desired glycosylated product enone **2a**. Further enone on treatment with $NaBH_4/CeCl_3$ under Luche reduction conditions furnished allylic alcohol **2b.** Further, alcohol was protected as C-4 hexanoate using $C_5H_{11}COOH$/DCC to provide **2c** and finally Upjohn dihydroxylation (OsO_4/NMO)[17-21] provided the desired monosaccharide diol (**2d**) in excellent yield (Scheme 3). Next, the regioselective installation of the incoming glycosyl donor at the C-3 position of diol **2d** initially started with a tin-mediated regioselective glycosylation using stoichiometric dibutyltin oxide (Bu_2SnO)[8-11] but yield and the reproducibility was major concern. Boron catalyst ($Ph_2BOCH_2CH_2NH_2$) was known to be successfully used towards the regioselective glycosylation by Taylor's group for excellent regioselectivity towards the carbohydrate motifs. [25-29]



Scheme 2a: Synthesis of key monosaccharide unit

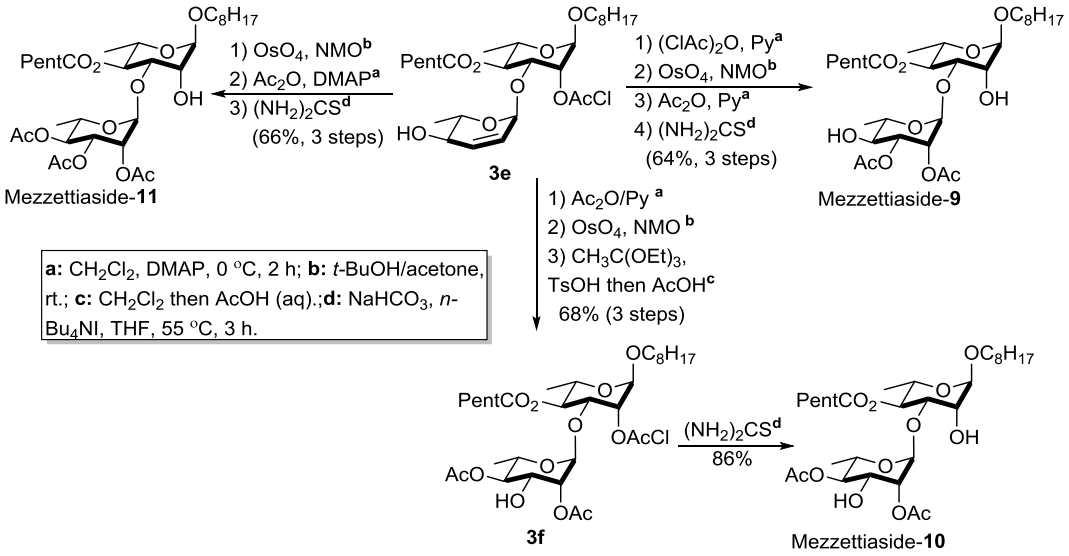
The desired mezzettiasides were synthesized exploiting the boron chemistry ($Ph_2BOCH_2CH_2NH_2$) and Palladium catalyzed glycosylation ($Pd_2(dba)_3{\cdot}CHCl_3/4PPh_3$) to get good C-3 regioselectivity/α-stereochemsitry. [3] In this regard, the diol (**2d**) on treatment with Pyranone **1.3** in presence of boron catalyst under palladium glycosylation conditions (30 mol% $Ph_2BOCH_2CH_2NH_2$/ 2.5 mol% $Pd(PPh_3)_2$), a good C-3:C-2 (7.5:1) regioselectivity and complete control of stereoselectivity was obtained.[3,6,13] Although the regiomers (**3a/3b**) were inseparable but were carried forward as it. Further, the mixture of enones (**3a/3b)** was protected as chloroacetate ($(ClAc)_2O$/pyridine) providing again an inseperable mixture of C-3:C-2 (**3c/3d**) followed by treatment with $NaBH_4/CeCl_3$ provided pure disaccharide allylic alcohol **3e** using column chromatography with excellent yield (Scheme 3).



Scheme 3: Synthesis of key intermediate

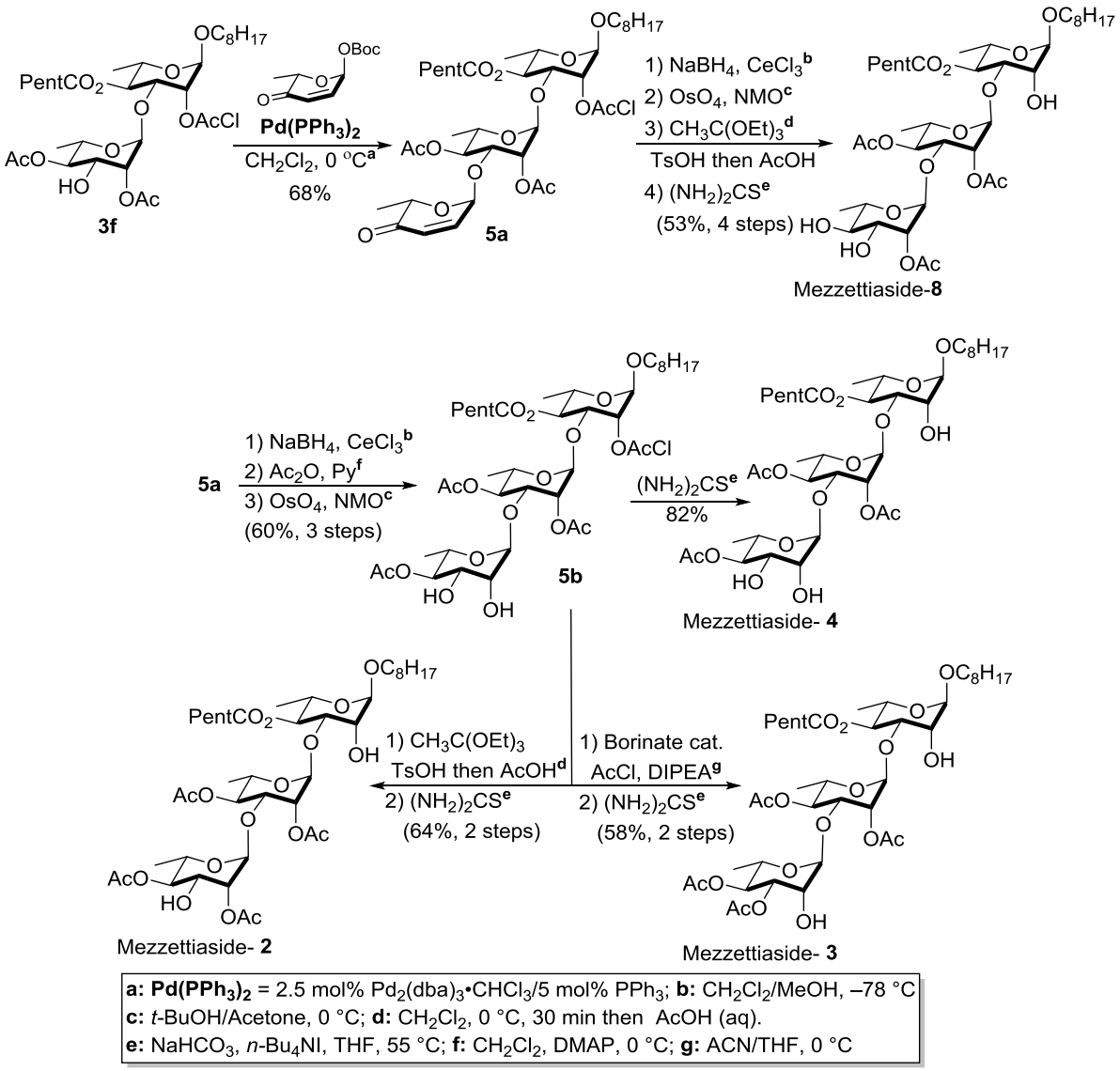
The allylic alcohol **3e** was further expanded into final three disaccharide mezzettiasides **9-11** (Scheme 4). Allylic alcohol upon treatment with chloroacetic anhydride/pyridine followed by Upjohn dihydroxylation (OsO_4/NMO), acylation (Ac_2O/DMAP) and finally deprotection of the chloroacetate group using thiourea $(NH_2)_2CS/NaHCO_3/n\text{-}Bu_4NI$[31] provided disaccharide mezzettiaside-**9**

Similarly, when the chloroacetate step was removed from the above sequence, mezzettiaisde-**11** was obtained in good yield. Mezzettiaside-**10** was synthesized from alcohol **3e** via C-4 acylation, dihydroxylation, regioselective acylation using triethylorthoacetate ($CH_3C(OEt)_3$/TsOH/AcOH to provide axial C-2 acetate intermediate **3f** and finally deprotection of chloroacetate (-AcCl) was achieved using thiourea conditions (Scheme 4).



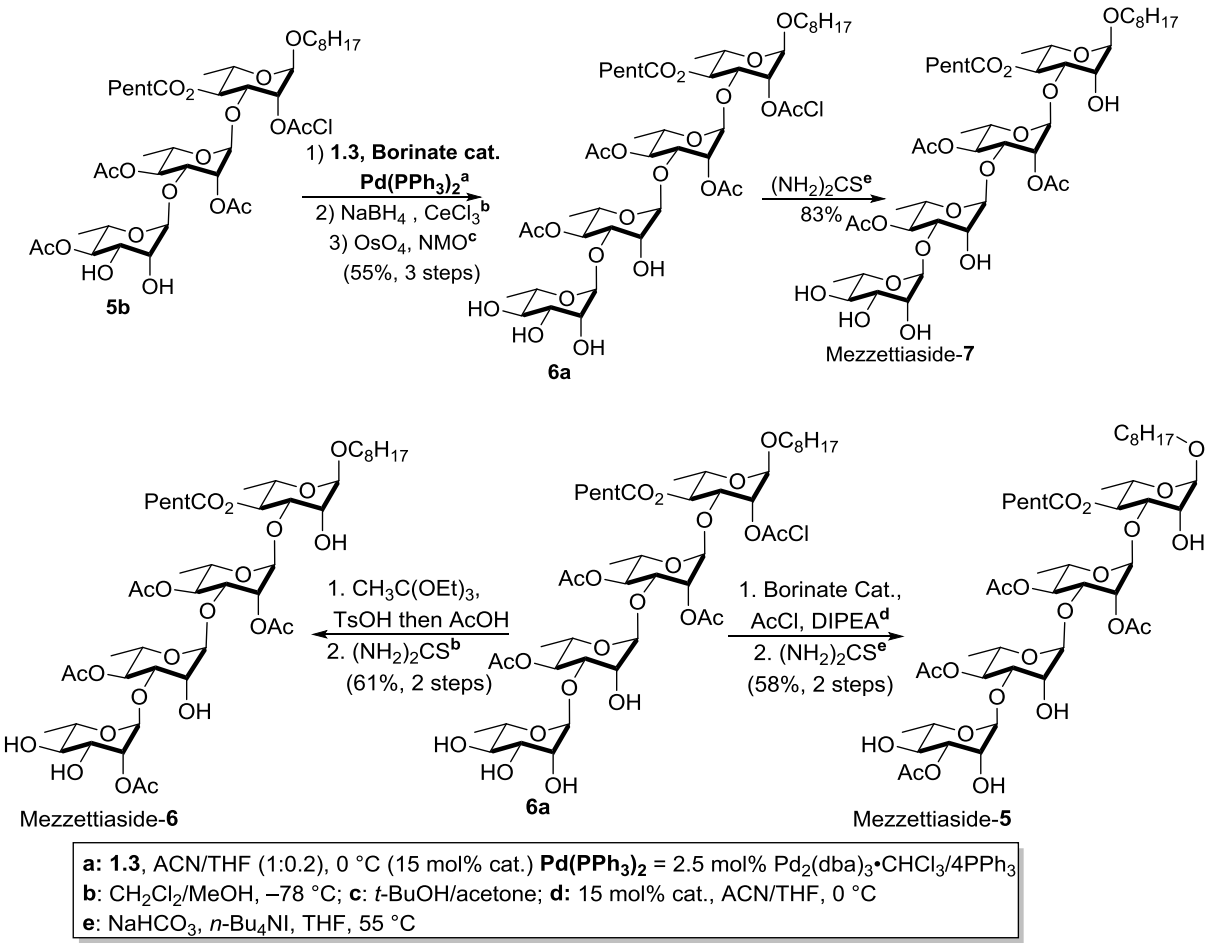
Scheme 4: Synthesis of mezzettiaside **9-11**

From the retrosynthetic analysis, the disaccharide alcohol **3f** served to be the starting point for the synthesis of trisaccharide mezzettiasides-**2-4**&**8**. Alcohol **3f** upon Pd-catalyzed glycosylation with Boc-Pyranone (**1.3**) provided trisaccharide enone **5a**. Enone was further diverged into 4 final compounds. For mezzettiaside-**8**, the enone underwent post-glycosylation transformations followed by orthoacetate chemistry to provide axial C-2 acetate using triethylorthoacetate/TsOH/AcOH and finally –ClAc group deprotection. For the synthesis of trisaccharides and tetrasaccharides mezzettiasides, intermediate **5a** was further exploited. Enone **5a** was utilized to obtain mezzettiaside-**4** via Luche reduction, acylation and dihydroxylation to provide key trisaccharide intermediate **5b** followed by removal of the protecting group. Regioselective C-3 acylation in mezzettiaside-**3** was achieved using ($Ph_2BOCH_2CH_2NH_2$/AcCl/DIPEA) on diol **5b** followed by the chloroacetate removal furnished mezzettiaside-**3** in good yield. Whereas, intermediate **5b** upon treatment with $CH_3C(OEt)_3$/TsOH/AcOH provided axial C-2 acetate and removal of the protecting group provided mezzettiaside-**2** (Scheme 5).



Scheme 5: Synthesis of mezzettiaside-**2**-**4**&**8**

Finally, the route to tetrasaccharide natural products was achieved via regioselective glycosylation of diol **5b** with α-L-Boc-Pyranone **1.3** under Pd-/B-mediated dual catalysis to provide tetrasaccharide enone, followed by post-glycosylation ($NaBH_4/OsO_4$) gave intermediate **6a**. Triol **6a** upon chloroacetate deprotection using thiourea/$NaHCO_3$ provided mezzettiaside-**7** in 83% yield. Once again, relying on the divergent approach when triol **6a** underwent regioselective C-3 acylation using boron catalyst in presence of acetyl chloride followed by deprotection provided mezzettiaside-**5**. Similarly, mezzettiaside-**6** was prepared using $CH_3C(OEt)_3$/TsOH/AcOH, and chloroacetate deprotection (Scheme 6).

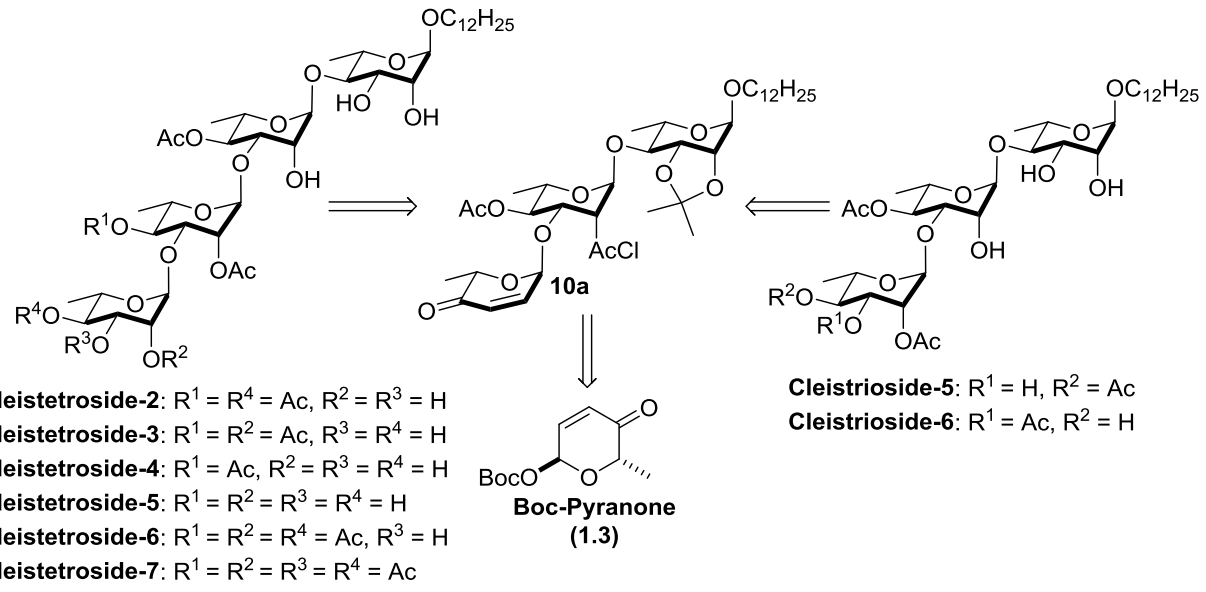


Scheme 6: Synthesis of Mezzettiasides-**5-7**

In conclusion, a series of 10 natural products was obtained in just 13-21 longest linear steps from Boc-Pyranone **1.3**. This first total synthesis required 41 overall steps with only one protecting group (AcCl) for the synthesis of 9 natural products and for the 10th natural product, the chloroacetate was utilized twice. The methodology developed is highly regio-/ stereo-selective and rely on electrophilic boron and nucleophilic Pd-catalyst.

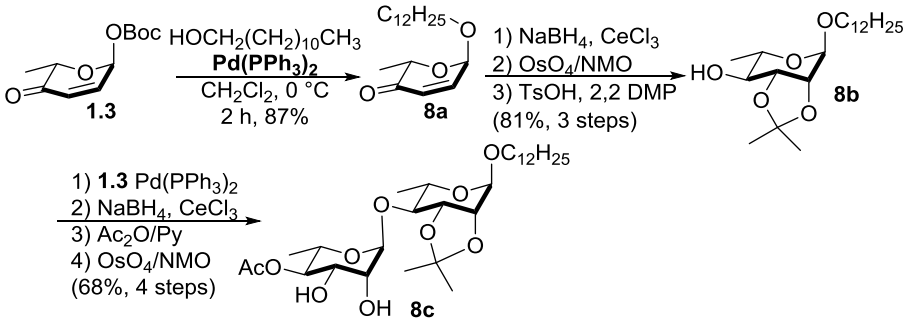
Application of Boc-pyranone in the Cleistrio-/Cleistetro-sides anti-cancer natural products:

Cleistriosides/Cleistetrosides are a family of oligosaccharide natural products containing *rhamno*-sugar connected via 1,4/1,3-linkage. These natural products were isolated from *Cleistopholis patens/glauca* and some are known to possess antimicrobial activity against methicillin-resistant *Staphylococcus aureus*, while others possess anti-cancer activity.[8-11] Utilizing asymmetric divergent approach, the synthesis of all the 8 highly complex natural products was completed using only two protecting groups starting from Boc-Pyranone **1.3** [5-7]. Once again, the pyranone has shown its wide application towards the synthesis of oligosaccharides. These natural products are divided into trisaccharides (Cleistriosides) while the tetrasaccharide are known as Cleistetrosides (Scheme 7).



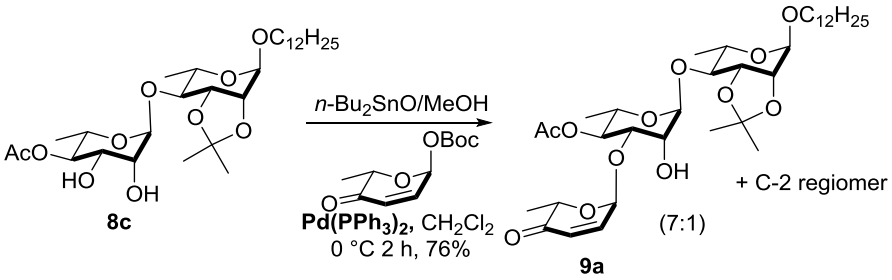
Scheme 7: General representation of Cleistetrosides/Cleistriosides

Retrosynthetically, cleistriosides/cleistetrosides natural products were planned from a common trisaccharide enone **10a**, whereas, enone was obtained from Boc-Pyranone's coupling with the disaccharide intermediate **8c** (overall 10 steps). The synthesis of natural products commenced with the treatment of Boc-Pyranone with dodecyl alcohol in presence of $Pd_2(dba)_3{\cdot}CHCl_3$ [14-21] conditions at 0 ^oC to provide corresponding enone **8a**. Enone **8a** underwent post-glycosylation transformations ($NaBH_4/OsO_4$) followed by acetonide protection using 2,2 dimethoxy propane DMP/TsOH provided glycosyl acceptor **8a**. Further alcohol **8b** under Pd-catalyzed condition reacted with a second equivalent of Boc-pyranone **1.3** furnished disaccharide enone. Enone upon $NaBH_4$ reduction, acylation (Ac_2O/Py) and Upjohn dihydroxylation provided disaccharide diol **8c** in overall good yield (Scheme 8). As can be seen from the structure, the sugar motifs are attached via 1,3 linkage, the acceptor **8c** has two reactive sites (C-3:C-2) for the glycosylation, towards the synthesis of Cleistrio-/Cleistetro-sides.



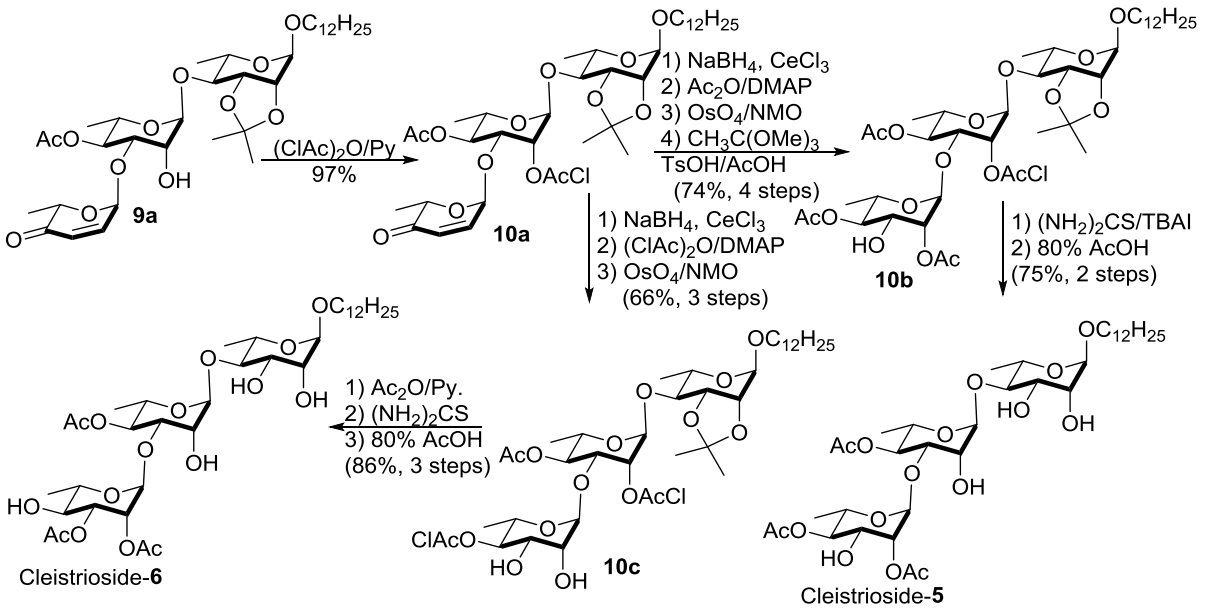
Scheme 8: Synthesis of intermediate diol

The key 1,3-linkage was achieved using tin-oxide chemistry which provided C-3 regioselective glycosylation in the 7:1 (C-3:C-2) ratio.[8] Diol upon treatment with dibutyltinoxide under reflux conditions provided tin-acetal complex which underwent glycosylation with Boc-pyraone using $Pd(PPh_3)_2$ in CH_2Cl_2 providing trisaccharide enone in 76% yield (Scheme 9).



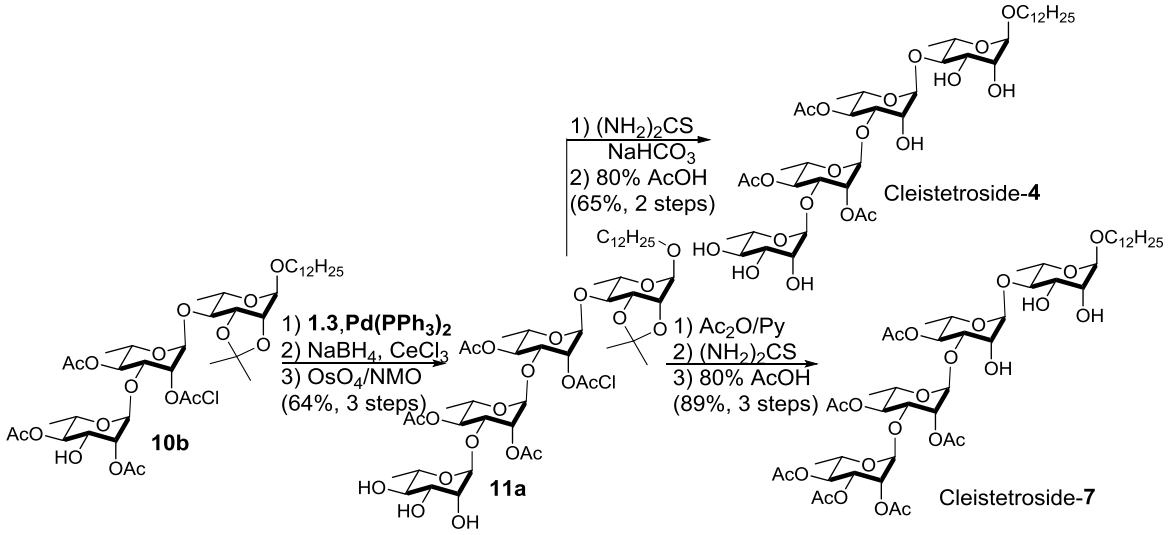
Scheme 9: Regioselective glycosylation using tinoxide

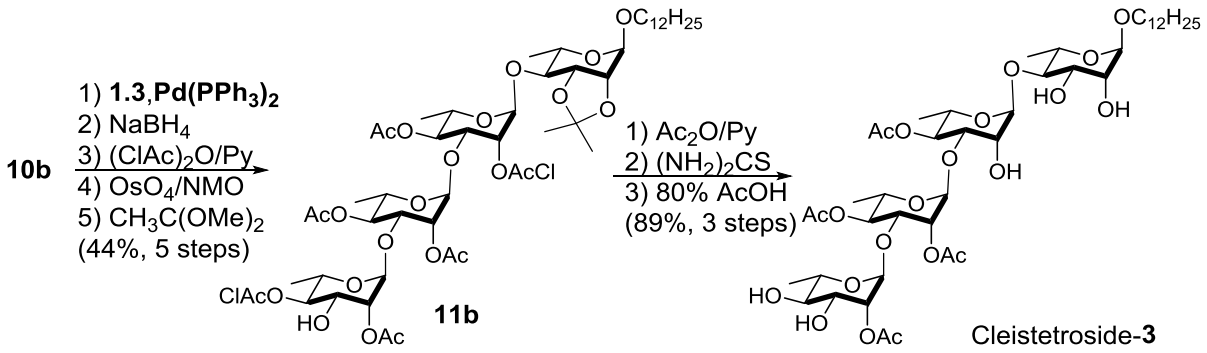
The hydroxyl group of the enone **9a** was protected as chloroacetate using $(ClAc)_2O$/Py and reduced under Luche reduction conditions (sodium borohydride, $NaBH_4/CeCl_3$), acylated (Ac_2O/DMAP), dihydroxylated (OsO_4/NMO)[14-16] followed by orthoacetate protection using triethylorthoacetate provided axial C-2 acetate. Finally removal of the chloroacetate and acetonide protecting groups using thiourea/$NaHCO_3$/n-Bu_4NI[31] and 80% AcOH respectively furnished Cleistrioside-**5** (Scheme 10). Similarly, enone **10a** was expanded to Cleistrioside-**6** using Luche reduction, chloroacylation(ClAc-), dihydroxylation (OsO_4/NMO) to provide diol **10c**. Diol was acylated (Ac_2O/Py) to provide bis-acetate and finally removal of acetonide/chloroacetate protecting groups provided cleistrioside-**6**. Intermediate **10b** was further utilized for a divergent approach to obtain Cleistetrosides. In this regards, alcohol **10b** upon treatment with Boc-pyranone **1.3** using palladium catalyzed glycosylation. Followed by post-glycosylation ($NaBH_4/OsO_4$) provided triol **11a** which upon acylation provided tetrasaccharide triacetate and finally deprotection of chloroacetate/acetonide provided Cleistetroside-**7**.



Scheme 10: Synthesis of Cleistrioside-**5**/**6**

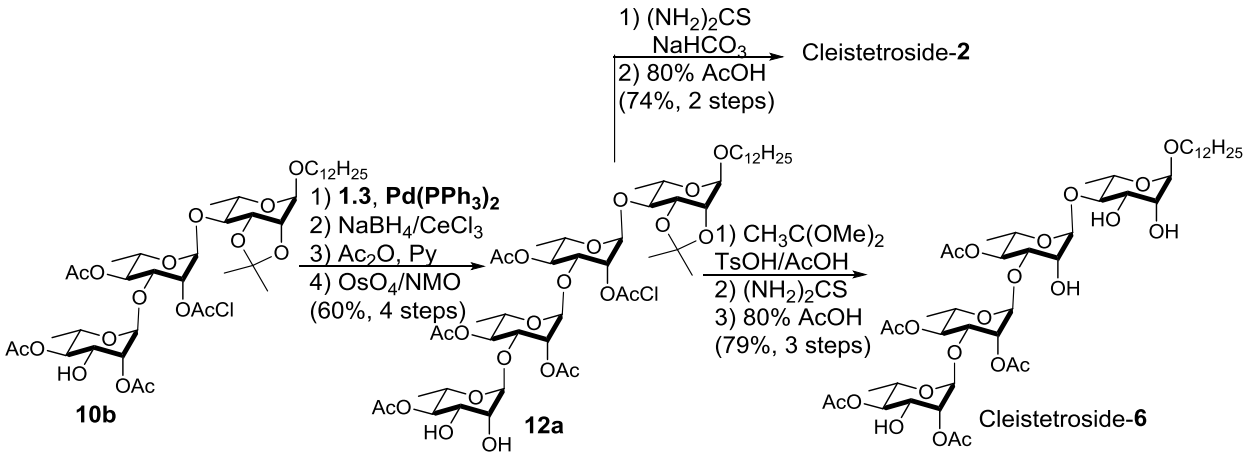
Alcohol **10b** underwent Pd $(PPh_3)_2$ glycosylation, Luche reduction, chloroacetate protection, dihyroxylation and orthoacetate to provide tetrasaccharide alcohol **11b**. Alcohol upon treatment with $(NH_2)_2CS$ and 80% AcOH provided cleistetroside-**3**, deprotection of triol **11a** using thiourea/80% AcOH provided Cleistetroside-**4** in good yield.

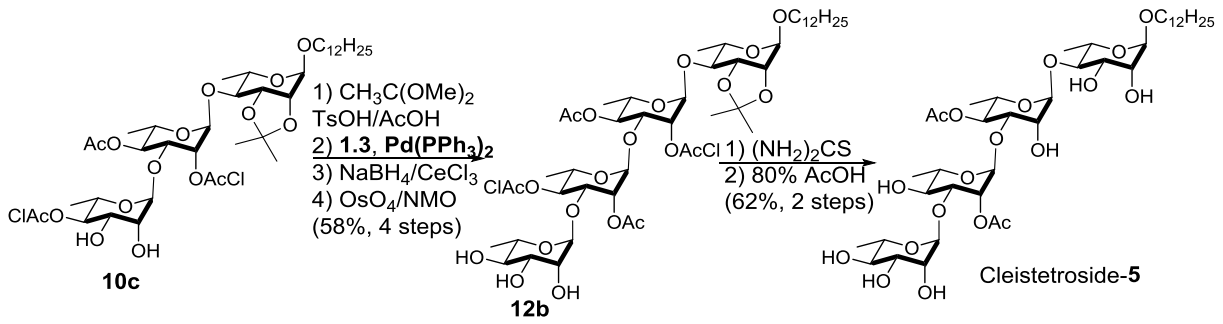




Scheme 11: Synthesis of Cleistetroside-**4/7/3**

The final three cleistetrosides were synthesized starting from alcohol **10b,** which upon palladium catalyzed glycosylation provided enone. The tetrasaccharide enone was reduced, acylated and diihydroxylated to provide diol **12a**. Diol **12a** was protected as C-2 acetate using triethylorthoacetate and finally deprotection provided Cleistetroside-**6**. In turn, trisaccharide intermediate **10c** on treatment with triethyl orthoacetate installed axial C-2 acetate followed by $Pd(PPh_3)_2$ mediated glycosylation with Boc-Pyranone then post-glycosylation conditions provided tetrasaccharide triol, which was deprotected to provide Cleistetroside-**5** in excellent yield. The final natural product, cleistetroside-**2** in the series was obtained from the intermediate diol **12a** via deprotection strategy.[8]





Scheme 12: Synthesis of Cleistetroside-**2/5/6**

Finally, eight highly complex natural products were synthesized using the asymmetric divergent approach. This synthesis featured the use of organotin for the regioselective glycosylation with only two type of protecting groups throughout the sequence.

Conclusion: Overall, Boc-Pyranones have shown tremendous potential as a glycosyl donor for glycosylation reactions and can be utilized towards the synthesis of natural/unnatural carbohydrate motifs possessing fascinating biological properties.

Acknowledgements
The author acknowledged no financial support.

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