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# $Zn(OTf)_2$ Promoted Rearrangement of 1,2-Cyclopropanated Sugars with Amines: A Convenient Method for the Synthesis of 3-Polyhydroxyalkyl-substituted Pyrrole Derivatives

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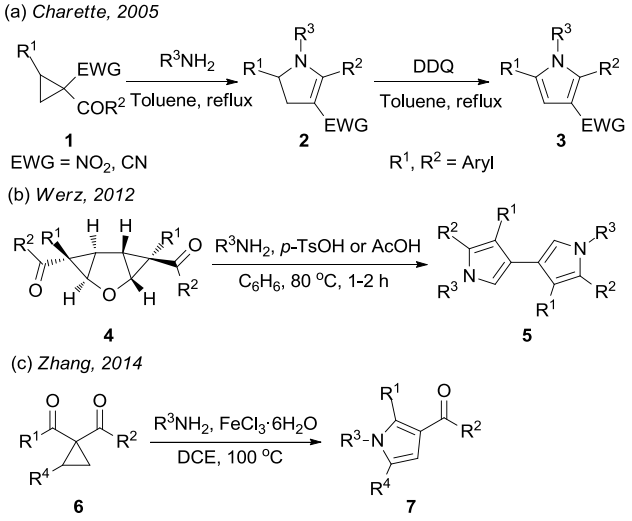
A rearrangement reaction of 1,2-cyclopropanated sugars with alkylamines or arylamines promoted by $Zn(OTf)_2$ is described. The method offers a series of 3-polyhydroxyalkyl-substituted pyrrole derivatives with multiple chiral centers in moderate to excellent yields. The epimerization is achieved by inverting the stereochemistry at the free hydroxyl group of the resulting pyrrole, which would give access to many more possible stereoisomers.

## Introduction

Pyrroles are an important class of heterocyclic compounds in organic chemistry.[1] The widespread occurrence of pyrrole-containing compounds in natural products,[2] pharmaceuticals,[3] and organic materials[4] has constantly stimulated organic and medicinal chemists to develop novel strategies for their synthesis and transformations.[5] Although a number of classical methods for constructing pyrrole rings including the Knorr,[6] Hantzsch,[7] and Paal–Knorr reaction[8] have been known for many years, the development of new approaches to afford pyrroles with multifunctional groups and several chiral centers still represents a challenge.

Donor-acceptor (D–A) cyclopropanes, which exhibit a high level of reactivity to a wide range of nucleophiles and electrophiles in the presence of a Lewis acid, have been widely applied to the construction of a variety of skeletons,[9] especially five-, six-, seven-membered carbocycles and heterocycles.[9a,9c] Among these, the development of valid protocols to access functionalized pyrrole derivatives from D–A cyclopropanes has attracted increasing interests from the chemical community.[10-13] Several literature procedures have been focused on the synthesis of the pyrrole ring via the cycloaddition of activated D–A cyclopropanes with imines,[1o] nitriles[11] and nitrones.[12] However, these methods either required stoichiometric promoters or needed multiple reaction steps.

On the other hand, the formation of functionalized pyrrole derivatives could be achieved by the rearrangement of D–A cyclopropanes with amines.[13] In 2005, Charette and co-workers[13b] reported the synthesis of 4-nitro- and 4-cyano-pyrroles **3** from doubly activated cyclopropanes **1** and amines with a stepwise procedure (Scheme 1, a). In 2012, Werz et al.[13d] developed a novel ring enlargement/aromatization domino approach to afford 3,3'-linked oligopyrroles **5** from ketone-substituted cyclopropanes **4** (Scheme 1, b). Recently, Zhang et al.[13f] presented the synthesis of multisubstituted pyrrole derivatives **7** involving an iron-mediated oxidation domino reaction of doubly activated cyclopropanes **6** with anilines (Scheme 1, c). These approaches have provided access to pyrroles bearing a variety of substituent groups effectively. Nevertheless, cyclopropanated carbohydrates have only rarely been used to prepare pyrrole derivatives with multichiral centers. To the best of our knowledge, only one example was reported by Zhang[14] in 2013, which introduced α-polyhydroxyalkyl-substituted pyrroles from 1,2-cyclopropa-3-pyranones with amines, although only pyranoses have been investigated. Inspiringly, these new *N*-substituted pyrroles




**Scheme 1.** Rearrangement Reactions of D–A Cyclopropanes with Amines

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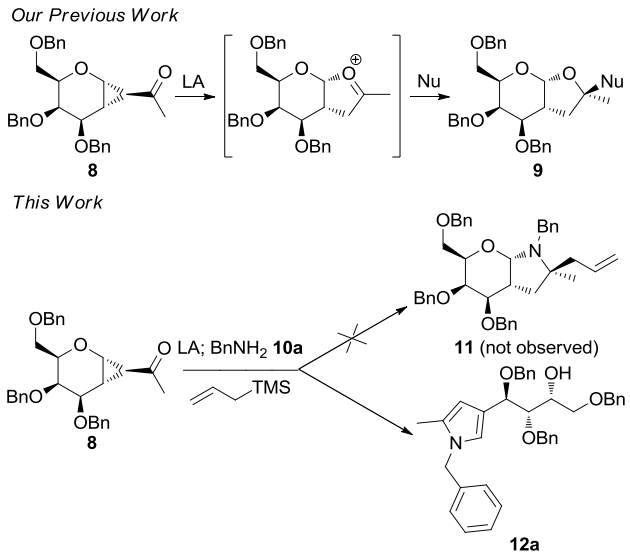



**Scheme 2.** Proposed Synthetic Route for 2,2-Di-substituted Pyrrolo[2,3-*b*]pyran Derivatives and the Experimental Result

exhibited moderate cytotoxicity against some cancer cell lines, especially vincristine-resistant KB/VCR cells. Thus, it is necessary to develop a convenient method to synthesize a greater variety of carbohydrate-based pyrroles.[15]

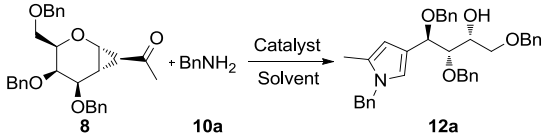
Herein, we disclose our results on the rearrangement of cyclopropanated sugars with alkylamines or arylamines catalyzed by $Zn(OTf)_2$, which affords a series of 3-polyhydroxyalkyl-substituted pyrrole derivatives with sidechains containing multiple stereogenic carbons.

## Results and discussion

Our initial attempts began with the cyclization reaction of galactose-derived 1,2-cyclopropanated sugar **8**,[16] $BnNH_2$ (**10a**) and allyltrimethylsilane in the presence of $BiCl_3$ in toluene for the preparation of **9** (Scheme 2).[17] We envisioned that 2,2-di-substituted pyrrolo[2,3-*b*]pyran derivative **11** can be obtained via a similar reaction. Unfortunately, the reaction was very complicated and no major product was detected by TLC analysis. To our surprise, after changing $BiCl_3$ into $BF_3{\cdot}OEt_2$ as a catalyst, we obtained pyrrole derivatives **12a** as a major product in 51% yield. The presence of the pyrrole ring in **12a** was partially evidenced by the $^{13}C$ ring carbon resonances of 107.2, 120.6, 121.6, 126.8 ppm which were consistent with the literature.[18] Since the product **12a** represented a new type of pyrrole, the reaction was further optimized by examining various conditions.

The screening studies were performed with 1,2-cyclopropanated sugar **8** and $BnNH_2$ (**10a)** as model substrates. As shown in Table 1, the coupling of 1,2-cyclopropanated sugar **8** and $BnNH_2$ (**10a)** promoted by $BF_3{\cdot}OEt_2$ or TMSOTf in toluene at room temperature could smoothly afford the desired pyrrole derivative **12a** in 51% or 45% yield, respectively (Table 1, entries 1-2). Also, with $InCl_3$ and $Cu(OTf)_2$, the product **12a** could be obtained in moderate yield (Table 1, entries 3-4). Some other Lewis acids such as $ZnCl_2$, $BiBr_3$, and AgOTf gave no conversion or produced trace amounts of **12a**

**Table 1.** Screening Studies of Rearrangement Reaction of 1,2-Cyclopropanated Sugar **8** with $BnNH_2$ (**10a**)[a]




| entry | catalyst | solvent | time (h) | yield (%)[b] |
|---|---|---|---|---|
| 1 | $BF_3{\cdot}OEt_2$ | Toluene | 12 | 51 |
| 2 | TMSOTf | Toluene | 12 | 45 |
| 3 | $InCl_3$ | Toluene | 12 | 41 |
| 4 | $Cu(OTf)_2$ | Toluene | 12 | 55 |
| 5 | $ZnCl_2$ | Toluene | 12 | 0 |
| 6 | $BiBr_3$ | Toluene | 12 | trace |
| 7 | AgOTf | Toluene | 12 | trace |
| 8 | $Zn(OTf)_2$ | Toluene | 12 | 64 |
| 9 | $Zn(OTf)_2$ | $CH_2Cl_2$ | 6 | 82 |
| 10 | $Zn(OTf)_2$ | $CHCl_3$ | 8 | 56 |
| 11 | $Zn(OTf)_2$ | 1,2-Dichloroethane | 8 | 74 |
| 12 | $Zn(OTf)_2$ | THF | 6 | 76 |
| 13 | $Zn(OTf)_2$ | Dioxane | 8 | 52 |
| 14 | $Zn(OTf)_2$ | $CH_3CN$ | 6 | 72 |
| 15 | $Zn(OTf)_2$ | DMSO | 12 | 27 |
| 16[c] | $Zn(OTf)_2$ | $CH_2Cl_2$ | 8 | 78 |
| **17**[d] | **$Zn(OTf)_2$** | **$CH_2Cl_2$** | **4** | **82** |
| 18[e] | $Zn(OTf)_2$ | $CH_2Cl_2$ | 12 | 67 |

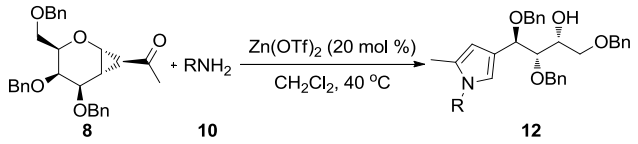
[a] Reactions were performed with 0.10 mmol of sugar, 0.20 mmol of $BnNH_2$ and 30 mol % of catalyst in 1.0 mL of solvent at room temperature unless otherwise noted; [b] Isolated yield; [c] 20 mol % of catalyst was used; [d] 20 mol % of catalyst was used at 40 °C; [e] 10 mol % of catalyst was used at 40 °C.

(entries 5-7). Further screening studies revealed that $Zn(OTf)_2$ gave the product in the highest yield (Table 1, entry 8). Subsequently, other reaction parameters were investigated with $Zn(OTf)_2$. A screening of different solvents showed that dichloromethane was the most suitable solvent for this transformation (Table 1, entries 9-15). When the catalyst loading was lowered from 30 mol % to 20 mol %, the yield slightly decreased (Table 1, entry 16). To our delight, the pyrrole derivative **12a** could be isolated in 82% yield using 20 mol % of $Zn(OTf)_2$ after elevating the temperature to a refluxing condition (Table 1, entry 17). Further decreasing of the catalyst loading caused a decline of the product yield (Table 1, entry 18).

Under the optimized reaction conditions, the scope of substrates was investigated (Table 2). Firstly, various benzylamines including $BnNH_2$ (**10a**), 4-methoxybenzylamine (**10b**) and (*S*)-α-phenethylamine (**10c**) reacted with 1,2-cyclopropanated sugar **8** to give the corresponding products in good yields (Table 2, entries 1-3). It was also pleasing that bulky diphenylmethanamine (**10d**) could be employed in the coupling reaction to afford the pyrrole derivative **12d** in 83% yield. Similarly, treatment of 1,2-cyclopropanated sugar **8** with linear (**10e**), branched (**10g**), cyclic (**10h**) and even long-chain (**10f**) alkylamines in the presence of $Zn(OTf)_2$ could smoothly afford the desired pyrrole derivatives in good yields (Table 2,

entries 5-8). However, no reaction occurred when *tert*-butylamine (**10i**) was used, possibly due to unfavorable steric hindrance (Table 2, entry 9). Satisfactorily, other functional aliphatic amines such as allylamine (**10j**), propargylamine (**10k**),

**Table 2.** $Zn(OTf)_2$ Promoted Rearrangement Reactions of 1,2-Cyclopropanated Sugar **8** with Amines **10**[a]




8 10 12

| entry | R | product | time (h) | yield (%)[b] |
|---|---|---|---|---|
| 1 | Benzyl (**10a**) | **12a** | 4 | 82 |
| 2 | 4-Methoxybenzyl (**10b**) | **12b** | 4 | 76 |
| 3 | (*S*)-*α*-Phenethyl (**10c**) | **12c** | 8 | 88 |
| 4 | 1,1-Diphenylmethyl (**10d**) | **12d** | 15 | 83 |
| 5 | *n*-Butyl (**10e**) | **12e** | 4 | 77 |
| 6 | *n*-Octyl (**10f**) | **12f** | 4 | 82 |
| 7 | *i*-Butyl (**10g**) | **12g** | 4 | 84 |
| 8 | Cyclohexyl (**10h**) | **12h** | 18 | 80 |
| 9 | *t*-Butyl (**10i**) | **12i** | 48 | 0 |
| 10 | Allyl (**10j**) | **12j** | 4 | 81 |
| 11 | Propargyl (**10k**) | **12k** | 4 | 48 |
| 12 | 3-Methoxypropyl (**10l**) | **12l** | 4 | 83 |
| 13 | $RNH_2$ = (*S*)-methyl 2-amino-3-phenylpropanoate (**10m**) | **12m** | 24 | 85 |
| 14 | Ph (**10n**) | **12n** | 12 | 73 |
| 15 | 4-$MeOC_6H_4$ (**10o**) | **12o** | 12 | 78 |
| 16 | 4-$PhC_6H_4$ (**10p**) | **12p** | 12 | 72 |
| 17 | *p*-Toluenesulfonamide (**10q**) | **12q** | 12 | 0 |

[a] Reactions were performed with 0.10 mmol of sugar, 0.20 mmol of amines and 20 mol % of $Zn(OTf)_2$ in 1.0 mL of $CH_2Cl_2$ at 40 °C unless otherwise noted; [b] Isolated yield.

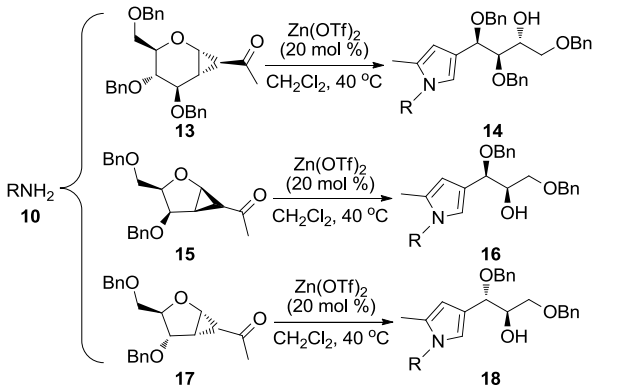
3-methoxypropan-1-amine (**10l**) and (*S*)-methyl 2-amino-3-phenylpropanoate (**10m**) could be used in the reaction (Table 2, entris 10-13). In addition, coupling of 1,2-cyclopropanated sugar **8** and arylamines such as phenylamine (**10n**), 4-methoxyaniline (**10o**) and 4-phenylbenzenamine (**10p**) under the optimized reaction conditions also gave the desired pyrrole in good yields (Table 2, entries 14-16). Whereas, it was found that *p*-toluenesulfonamide (**10q**) was unsuitable for this transformation possibly as a result of its poor nucleophilicity (Table 2, entry 17).

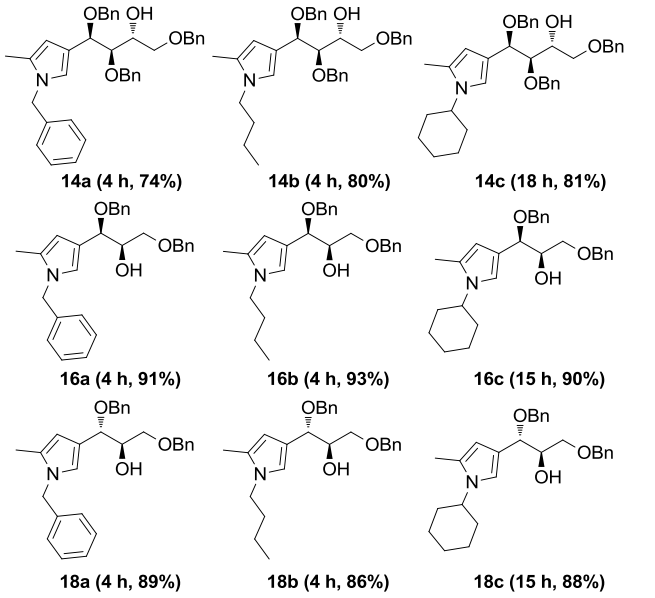
Next, the generality of the reaction was further explored by reacting alkylamines with other cyclopropanated sugars under the standard conditions. As illustrated in Table 3, treatment of 1,2-cyclopropanated glucose **13**[19] with benzyl, linear aliphatic, and cyclic aliphatic amines in the presence of $Zn(OTf)_2$ could smoothly afford the pyrrole derivatives **14** in good yields. To our delight, in addition to 1,2-cyclopropanated pyranoses, furanosyl 1,2-cyclopropanated ketones **15**[19] and **17**[20] proved to be amenable to this transformation, which provided corresponding pyrrole derivatives **16** and **18** in good to excellent yields under the same conditions, respectively.

Moreover, we intended to explore the transformation of the products by inverting the stereochemistry at the free hydroxyl group of the obtained pyrroles. For instance, after the conversion of alcohol **12n** into the corresponding triflate, nucleophilic displacement of the triflyloxy group with $NaNO_2$ in *N*,*N*-dimethylformamide (DMF) at room temperature provided the epimer **19** in 26% yield over two steps (Scheme 3).[21]

On the basis of the experimental results, a plausible mechanism for the formation of pyrroles from 1,2-

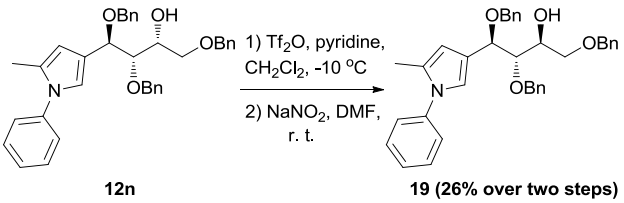
**Table 3.** $Zn(OTf)_2$ Promoted Rearrangement reactions of 1,2-Cyclopropanated Sugars **14, 16, 18** with Amines **10**[a]




[a] Reactions were performed with 0.10 mmol of sugars, 0.20 mmol of amines and 20 mol % of $Zn(OTf)_2$ in 1.0 mL of $CH_2Cl_2$ at 40 °C unless otherwise noted; [b] Isolated yield.

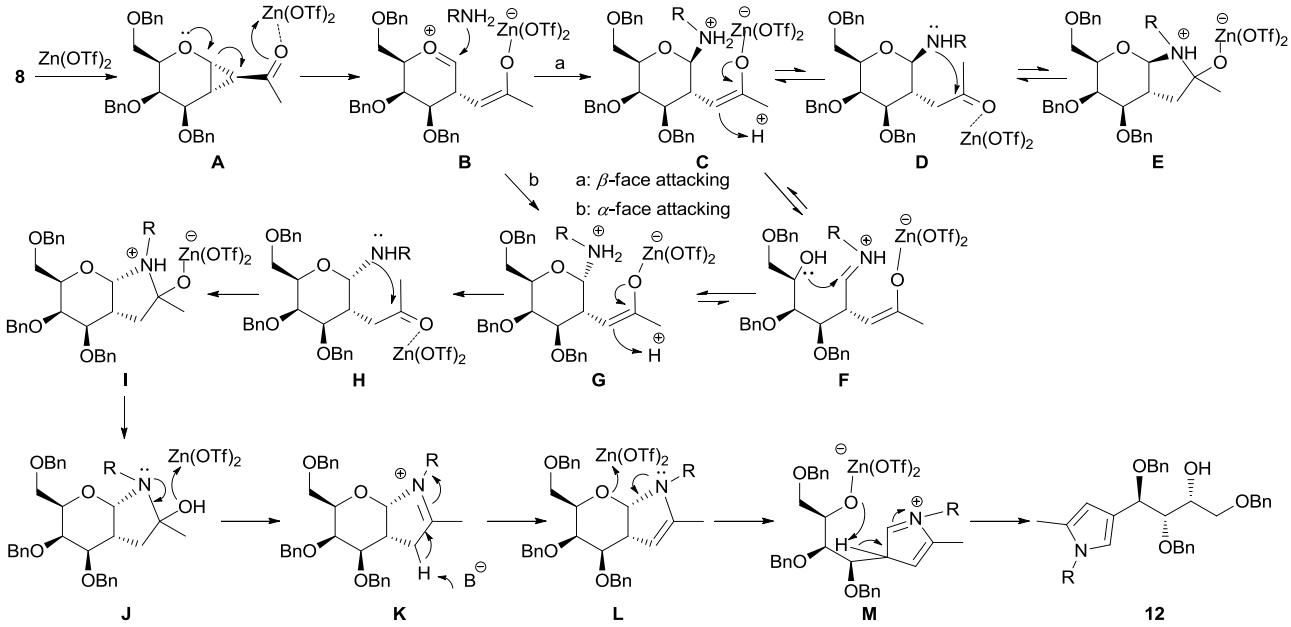
**Scheme 3.** Epimerization of Pyrrole **12n**




**12n** **19 (26% over two steps)**

cyclopropanated sugars is outlined in Scheme 4. Firstly, $Zn(OTf)_2$ could coordinate to the carbonyl oxygen and activate

the 1,2-cyclopropanated sugar **8** to cause the ring opening of cyclopropane to form awitterionic intermediate **B**. Then the amine was postulated to make a nucleophilic attack on the anomeric carbon from the β- or α-face to yield the 1,2-*trans*-configured intermediate **C** and 1,2-*cis*-configured intermediate **G**, respectively. Subsequently, the nitrogen atom on the




**Scheme 4.** A Plausible Mechanism of $Zn(OTf)_2$ Promoted Rearrangement Reaction of 1,2-Cyclopropanated Sugar with Amine

anomeric carbon could attack intramolecularly the carbonyl group to afford six-five fused ring intermediate **E** and **I**. Our previous study showed that a *cis*-configured six-five fused ring was more stable than a *trans* one.[17] Thus, the formation of 1,2-*trans*-configured bicyclic intermediate **E** was not dominant, and it would invert to form 1,2-*cis*-configured bicyclic intermediate **I** through anomerization. Then bicyclic intermediate **I** was futher converted to intermediate **L** via proton translocation and dehydration. Finally, elimination of intermediate **L** would achieve the pyrrole derivative **12**.

## Conclusions

We have developed a rearrangement reaction of cyclopropanated sugars with alkylamines and arylamines promoted by 20 mol % of $Zn(OTf)_2$. This methodology is efficient and allows access to polyhydroxylalkyl-substituted pyrrole derivatives containing 2-3 stereogenic centers from different 1,2-cyclopropanated sugars under mild condition. Furthermore, epimerization of the resulting pyrroles would give access to stereoisomers. Investigations into the biological activities of these compounds will be undertaken.

## Experimental section

### General information

All reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. Thin-layer chromatography was performed using silica gel GF254 precoated plates (0.20-0.25 mm thickness) with a fluorescent indicator. Visualization on TLC was achieved by UV light (254 nm) and a typical TLC indication solution (5% sulfuric acid / ethanol solution). Column chromatography was performed on silica gel 90, 200-300 mesh. Optical rotations were measured with a Perkin Elmer M341 Digital Polarimeter. $^1$H and $^{13}$C NMR (400 and 100 MHz, respectively) spectra were recorded on a Bruker Avance 400 spectrometer. $^1$H NMR chemical shifts are reported in ppm (δ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$, δ 7.26 ppm; DMSO-$d_6$, δ 2.50 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz) and integration. $^{13}$C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$, δ 77.0 ppm; DMSO-$d_6$, δ 39.5 ppm). HRMS electrospray (ESI) spectra were recorded with a BioTOF Q instrument.

### General procedure for the synthesis of pyrroles 12, 14, 16 and 18.

To a solution of amine **10** (0.200 mmol) in $CH_2Cl_2$ (1.0 mL) was added an appropriate 1,2-cyclopropanated sugar (**8**, **13**, **15**, **17**) (0.100 mmol). Then $Zn(OTf)_2$ (7.3 mg, 0.020 mmol) was added to the reaction mixture. The reaction mixture was stirred at 40 °C until the reaction was completed as detected by TLC. Then the reaction was quenched with a vigorously stirred solution of saturated aqueous $NaHCO_3$ (10 mL), and extracted with $CH_2Cl_2$ (3 × 10 mL). The organic layer was dried over $Na_2SO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (ethyl acetate/ petroleum ether = 1:6 to 1:15) to afford the corresponding pyrrole product.

**(2*R*,3*S*,4*R*)-4-(1-benzyl-5-methyl-1*H*-pyrrol-3-yl)-1,3,4-tris(benzyloxy)butan-2-ol (12a).** Obtained as a colorless syrup

(46.3 mg, 82%); $[\alpha]_D^{25}$ -27.0 (*c* 0.40, EtOAc); $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.35–7.15 (m, 16H), 7.11–7.04 (m, 2H), 7.03–6.95 (m, 2H), 6.81 (d, *J* = 1.5 Hz, 1H), 5.94 (s, 1H), 5.07 (s, 2H), 4.45 (m, 5H), 4.27 (d, *J* = 11.9 Hz, 1H), 4.24 (s, 2H), 4.10–4.00 (br, 1H), 3.63 (d, *J* = 7.6 Hz, 1H), 3.48 (t, *J* = 8.0 Hz, 1H), 3.41 (t, *J* = 8.0 Hz, 1H), 2.07 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 139.6, 139.4, 138.9, 128.9, 128.8, 128.7, 128.6, 128.4, 128.2, 128.1, 127.9, 127.7, 127.6, 127.5, 126.8, 121.6, 120.6, 107.2, 82.0, 74.6, 74.1, 72.8, 71.8, 69.3, 69.1, 49.9, 12.3; ESI-HRMS: m/z calcd for $C_{37}H_{39}NNaO_4$ $[M + Na]^+$: 584.2771; found: 584.2770.

**(2*R*,3*S*,4*R*)-1,3,4-tris(benzyloxy)-4-(1-(4-methoxybenzyl)-5-methyl-1*H*-pyrrol-3-yl)butan-2-ol (12b).** Obtained as a colorless syrup (44.9 mg, 76%); $[\alpha]_D^{25}$ -17.5 (*c* 0.32, EtOAc); $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.42–7.18 (m, 13H), 7.08 (d, *J* = 2.9 Hz, 2H), 6.96 (d, *J* = 7.9 Hz, 2H), 6.79 (s, 1H), 6.74 (d, *J* = 8.1 Hz, 2H), 5.94 (s, 1H), 4.98 (s, 2H), 4.55–4.40 (m, 5H), 4.29 (d, *J* = 12.1 Hz, 1H), 4.24 (s, 2H), 4.15–4.03 (br, 1H), 3.68 (s, 3H), 3.64 (d, *J* = 5.7 Hz, 1H), 3.54–3.46 (m, 1H), 3.46–3.40 (m, 1H), 2.09 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 158.7, 139.7, 139.4, 138.9, 131.2, 128.7, 128.2, 128.0, 127.9, 127.7, 127.5, 121.4, 120.5, 114.3, 107.1, 82.0, 74.6, 74.0, 72.8, 71.8, 69.3, 69.0, 55.5, 49.4, 12.4; ESI-HRMS: m/z calcd for $C_{38}H_{41}NNaO_5$ $[M + Na]^+$: 614.2877; found: 614.2875.

**(2*R*,3*S*,4*R*)-1,3,4-tris(benzyloxy)-4-(5-methyl-1-((S)-1-phenylethyl)-1*H*-pyrrol-3-yl)butan-2-ol (12c).** Obtained as a colorless syrup (48.0 mg, 82%); $[\alpha]_D^{25}$ -34.8 (*c* 0.40, EtOAc); $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.38–7.19 (m, 13H), 7.06 (d, *J* = 6.5 Hz, 2H), 6.67 (s, 1H), 5.86 (s, 1H), 4.52–4.36 (m, 5H), 4.23 (t, *J* = 12.4 Hz, 2H), 4.17 (d, *J* = 10.7 Hz, 1H), 4.10–4.00 (br, 1H), 3.77 (t, *J* = 6.8 Hz, 2H), 3.60 (d, *J* = 7.7 Hz, 1H), 3.48 (t, *J* = 7.6 Hz, 1H), 3.42 (m, *J* = 7.6 Hz, 1H), 2.17 (s, 3H), 1.65–1.50 (br, 2H), 1.27–1.09 (br, 10H), 0.82 (t, *J* = 6.7 Hz, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 139.7, 139.4, 138.9, 128.7, 128.5, 128.3, 128.2, 127.9, 127.7, 127.6, 127.5, 120.6, 120.1, 106.5, 82.2, 74.7, 74.1, 72.8, 71.8, 69.2, 69.0, 46.2, 31.7, 31.4, 29.1, 26.5, 22.5, 14.4, 12.3; ESI-HRMS: m/z calcd for $C_{38}H_{49}NNaO_4$ $[M + Na]^+$: 606.3554; found: 606.3557.

**(2*R*,3*S*,4*R*)-4-(1-benzhydryl-5-methyl-1*H*-pyrrol-3-yl)-1,3,4-tris(benzyloxy)butan-2-ol (12d).** Obtained as a colorless syrup (52.9 mg, 83%); $[\alpha]_D^{25}$ -26.3 (*c* 0.40, EtOAc); $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.42–7.18 (m, 19H), 7.09–7.00 (m, 6H), 6.64 (s, 1H), 6.25 (s, 1H), 6.01 (s, 1H), 4.51–4.42 (m, 3H), 4.42–4.33 (m, 2H), 4.24 –4.20 (m, 3H), 4.07–4.00 (br, 1H), 3.60 (dd, *J* = 7.7, 2.4 Hz, 1H), 3.47 (t, *J* = 7.9 Hz, 1H), 3.43–3.39 (m, 1H), 2.10 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 141.0, 139.5, 139.3, 138.8, 129.8, 129.0, 128.7, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6, 127.5, 120.3, 120.0, 107.4, 81.9, 74.4, 74.1, 72.8, 71.7, 69.2, 69.0, 63.0, 12.6; ESI-HRMS: m/z calcd for $C_{43}H_{43}NNaO_4$ $[M + Na]^+$: 660.3084; found: 660.3089.

**(2*R*,3*S*,4*R*)-1,3,4-tris(benzyloxy)-4-(1-butyl-5-methyl-1*H*-pyrrol-3-yl)butan-2-ol (12e).** Obtained as a colorless syrup (40.6 mg, 77%); $[\alpha]_D^{25}$ -38.5 (*c* 0.40, EtOAc); $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.39–7.19 (m, 13H), 7.06 (d, *J* = 6.9 Hz, 2H), 6.67 (d, *J* = 1.5 Hz, 1H), 5.86 (s, 1H), 4.51–4.36 (m, 5H), 4.24 (t, *J* = 10.4 Hz, 2H), 4.17 (d, *J* = 10.8 Hz, 1H), 4.10–4.00 (br, 1H), 3.77 (t, *J* = 7.0 Hz, 2H), 3.60 (d, *J* = 7.7 Hz, 1H), 3.48 (t, *J* = 7.9 Hz, 1H), 3.42 (t, *J* = 7.1 Hz, 1H), 2.17 (s, 3H), 1.63–1.51 (m, 2H), 1.28–1.16 (m, 2H), 0.83 (t, *J* = 7.4 Hz, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 139.7, 139.4, 138.9, 128.7, 128.5, 128.3, 128.2, 127.9, 127.7, 127.6, 127.5, 120.6, 120.1, 106.4, 82.1, 74.7, 74.1, 72.8, 71.8, 69.3, 69.1, 45.9, 33.5, 19.7, 14.1, 12.3; ESI-HRMS: m/z calcd for $C_{34}H_{41}NNaO_4$ $[M + Na]^+$: 550.2928; found: 550.2930.

**(2*R*,3*S*,4*R*)-1,3,4-tris(benzyloxy)-4-(5-methyl-1-octyl-1*H*-pyrrol-3-yl)butan-2-ol (12f).** Obtained as a colorless syrup (48.0 mg, 82%); $[\alpha]_D^{25}$ -34.8 (*c* 0.40, EtOAc); $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.38–7.19 (m, 13H), 7.06 (d, *J* = 6.5 Hz, 2H), 6.67 (s, 1H), 5.86 (s, 1H), 4.52–4.36 (m, 5H), 4.23 (t, *J* = 12.4 Hz 2H), 4.17 (d, *J* = 10.7 Hz, 1H), 4.10–4.00 (br, 1H), 3.77 (t, *J* = 6.8 Hz, 2H), 3.60 (d, *J* = 7.7 Hz, 1H), 3.48 (t, *J* = 7.6 Hz, 1H), 3.42 (m, *J* = 7.6 Hz, 1H), 2.17 (s, 3H), 1.65–1.50 (br, 2H), 1.27–1.09 (br, 10H), 0.82 (t, *J* = 6.7 Hz, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 139.7, 139.4, 138.9, 128.7, 128.5, 128.3, 128.2, 127.9, 127.7, 127.6, 127.5, 120.6, 120.1, 106.5, 82.2, 74.7, 74.1, 72.8, 71.8, 69.2, 69.0, 46.2, 31.7, 31.4, 29.1, 26.5, 22.5, 14.4, 12.3; ESI-HRMS: m/z calcd for $C_{38}H_{49}NNaO_4$ $[M + Na]^+$: 606.3554; found: 606.3557.

**(2*R*,3*S*,4*R*)-1,3,4-tris(benzyloxy)-4-(1-isobutyl-5-methyl-1*H*-pyrrol-3-yl)butan-2-ol (12g).** Obtained as a colorless syrup (44.3 mg, 84%); $[\alpha]_D^{25}$ -41.2 (*c* 0.40, EtOAc); $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.42–7.17 (m, 13H), 7.09 (s, 2H), 6.65 (s, 1H), 5.87 (s, 1H), 4.55–4.35 (m, 5H), 4.30–4.17 (m, 3H), 4.10–4.00 (br, 1H), 3.70–3.53 (m, 3H), 3.50–3.40 (m, 2H), 2.17 (s, 3H), 1.99–1.78 (m, 1H), 0.81 (s, 6H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 139.7, 139.4, 138.9, 128.7, 128.5, 128.3, 128.2, 128.1, 127.9, 127.7, 127.6, 127.5, 121.2, 120.0, 106.5, 82.1, 74.7, 74.1, 73.0, 71.8, 69.2, 69.1, 53.6, 30.2, 20.1, 12.5; ESI-HRMS: m/z calcd for $C_{34}H_{41}NNaO_4$ $[M + Na]^+$: 550.2928; found: 550.2930.

**(2*R*,3*S*,4*R*)-1,3,4-tris(benzyloxy)-4-(1-cyclohexyl-5-methyl-1*H*-pyrrol-3-yl)butan-2-ol (12h).** Obtained as a colorless syrup (44.5 mg, 80%); $[\alpha]_D^{25}$ -39.5 (*c* 0.40, EtOAc); $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.45–7.13 (m, 13H), 7.02 (s, 2H), 6.74 (s, 1H), 5.85 (s, 1H), 4.55–4.38 (m, 4H), 4.30–4.18 (m, 2H), 4.13 (d, *J* = 10.3 Hz, 1H), 4.06 (s, 1H), 3.78 (s, 1H), 3.60 (s, 1H), 3.55–3.40 (m, 3H), 2.19 (s, 3H), 1.91–1.70 (m, 4H), 1.70–1.59 (m, 1H), 1.59–1.50 (m, 1H), 1.49–1.30 (m, 3H), 1.25–1.10 (m, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 139.9, 139.8, 139.2, 128.6, 128.5, 128.4, 128.0, 127.9, 127.7, 127.5, 127.4, 119.7, 115.7, 105.6, 85.9, 77.0, 74.7, 72.6, 72.1, 70.3, 69.8, 54.5, 34.4, 34.2, 25.8, 25.5, 12.4; ESI-HRMS: m/z calcd for $C_{36}H_{43}NNaO_4$ $[M + Na]^+$: 576.3084; found: 576.3087.

**(2*R*,3*S*,4*R*)-4-(1-allyl-5-methyl-1*H*-pyrrol-3-yl)-1,3,4-tris(benzyloxy)butan-2-ol (12j).** Obtained as a colorless syrup (41.6 mg, 81%); $[\alpha]_D^{25}$ -29.0 (*c* 0.37, EtOAc); $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.55–7.21 (m, 13H), 7.07 (d, *J* = 6.0 Hz, 2H), 6.67 (s, 1H), 5.92 (s, 2H), 5.06 (d, *J* = 10.2 Hz, 1H), 4.79 (d, *J* = 16.9 Hz, 1H), 4.65–4.33 (m, 7H), 4.32–4.13 (m, 3H), 4.05 (s, 1H), 3.61 (d, *J* = 7.1 Hz, 1H), 3.45 (m, 2H), 2.14 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 139.7, 139.3, 138.9, 136.0, 128.7, 128.6, 128.3, 128.0, 127.9, 127.7, 127.5, 121.0, 120.3, 115.8, 106.7, 82.1, 74.7, 74.1, 72.8, 71.8, 69.3, 69.0, 48.8, 12.1; ESI-HRMS: m/z calcd for $C_{33}H_{37}NNaO_4$ $[M + Na]^+$: 534.2615; found: 534,2602.

**(2*R*,3*S*,4*R*)-1,3,4-tris(benzyloxy)-4-(5-methyl-1-(prop-2-yn-1-yl)-1*H*-pyrrol-3-yl)butan-2-ol (12k).** Obtained as a red syrup (24.4 mg, 48%); $[\alpha]_D^{25}$ -34.2 (*c* 0.36, EtOAc); $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.42–7.17 (m, 13H), 7.05 (d, *J* = 6.3 Hz, 2H), 6.78 (d, *J* = 1.5 Hz, 1H), 5.92 (s, 1H), 4.75 (d, *J* = 1.7 Hz, 2H), 4.51 (d, *J* = 6.5 Hz, 1H), 4.47 (d, *J* = 5.3 Hz, 2H), 4.42 (m, 2H), 4.27 (d, *J* = 11.9 Hz, 1H), 4.22 (d, *J* = 10.6 Hz, 1H), 4.14 (d, *J* = 10.5 Hz, 1H), 4.08–4.00 (m, 1H), 3.59 (dd, *J* = 7.9, 2.4 Hz, 1H), 3.50 (t, *J* = 8.0 Hz, 1H), 3.43 (m, 2H), 2.24 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 139.6, 139.2, 138.9, 128.8, 128.7, 128.6, 128.4, 128.3, 127.9, 127.7, 127.5, 120.7, 107.1, 82.0, 80.3, 75.7, 74.3, 72.9, 71.7, 69.5, 69.0, 36.0, 12.1; ESI-HRMS: m/z calcd for $C_{33}H_{35}NNaO_4$ [M + Na]$^+$: 532.2458; found: 532,2435.

**(2*R*,3*S*,4*R*)-1,3,4-tris(benzyloxy)-4-(1-(3-methoxypropyl)-5-methyl-1*H*-pyrrol-3-yl)butan-2-ol (12l).** Obtained as a colorless syrup (45.4 mg, 83%); $[\alpha]_D^{25}$ -25.0 (*c* 0.49, EtOAc); $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.35–7.23 (m, 13H), 7.06 (d, *J* = 6.7 Hz, 2H), 6.65 (s, 1H), 5.87 (s, 1H), 4.50–4.30 (m, 5H), 4.28–4.23 (m, 2H), 4.18 (d, *J* = 10.9 Hz, 1H), 4.06 (d, *J* = 6.0 Hz, 1H), 3.83 (t, *J* = 6.8 Hz, 2H), 3.61 (d, *J* = 7.8 Hz, 1H), 3.48 (t, *J* = 7.9 Hz, 1H), 3.42 (m, 1H), 3.26–3.08 (m, 5H), 2.17 (s, 3H), 1.82–1.79 (m, 2H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 139.7, 139.4, 138.9, 128.7, 128.6, 128.4, 128.3, 128.2, 127.9, 127.7, 127.6, 127.5, 120.5, 120.3, 106.5, 82.1, 74.7, 74.1, 72.8, 71.8, 69.3, 69.0, 68.9, 58.3, 43.0, 31.3, 12.2; ESI-HRMS: m/z calcd for $C_{34}H_{41}NNaO_5$ [M + Na]$^+$: 566.2877; found: 566,2864.

**(*S*)-methyl 2-(2-methyl-4-((1*R*,2*S*,3*R*)-1,2,4-tris(benzyloxy)-3-hydroxybutyl)-1*H*-pyrrol-1-yl)-3-phenylpropanoate (12m).** Obtained as a colorless syrup (53.9 mg, 85%); $[\alpha]_D^{25}$ -82.8 (*c* 0.54, EtOAc); $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.39–7.19 (m, 13H), 7.14–7.08 (m, 5H), 7.07–6.99 (m, 2H), 6.90 (d, *J* = 1.3 Hz, 1H), 5.73 (s, 1H), 5.02 (dd, *J* = 10.6, 5.1 Hz, 1H), 4.50 (d, *J* = 6.6 Hz, 1H), 4.43 (m, 3H), 4.32 (d, *J* = 11.8 Hz, 1H), 4.27–4.19 (m, 1H), 4.17–4.08 (m, 2H), 4.08–3.99 (m, 1H), 3.63–3.54 (m, 4H), 3.51–3.44 (m, 1H), 3.44–3.37 (m, 2H), 3.27 (dd, *J* = 13.8, 10.8 Hz, 1H), 1.86 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 171.1, 139.6, 139.3, 138.9, 137.3, 129.5, 128.7, 128.6, 128.5, 128.3, 127.9, 127.7, 127.6, 127.5, 127.0, 121.4, 118.5, 106.3, 82.0, 74.5, 74.2, 72.8, 71.7, 69.2, 68.9, 59.1, 52.7, 38.1, 12.2; ESI-HRMS: m/z calcd for $C_{40}H_{43}NNaO_6$ [M + Na]$^+$: 656.2983; found: 656,2964.

**(2*R*,3*S*,4*R*)-1,3,4-tris(benzyloxy)-4-(5-methyl-1-phenyl-1*H*-pyrrol-3-yl)butan-2-ol (12n).** Obtained as a colorless syrup (40.0 mg, 73%); $[\alpha]_D^{25}$ -21.0 (*c* 0.43, EtOAc); $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.49 (t, *J* = 7.7 Hz, 2H), 7.40–7.20 (m, 16H), 7.11–7.04 (m, 2H), 6.87 (s, 1H), 6.13 (s, 1H), 4.60–4.46 (m, 5H), 4.36 (d, *J* = 4.8 Hz, 1H), 4.33 (d, *J* = 3.8 Hz, 1H), 4.25 (d, *J* = 10.9 Hz, 1H), 4.13–4.04 (m, 1H), 3.68 (dd, *J* = 7.8, 2.3 Hz, 1H), 3.53 (t, *J* = 7.9 Hz, 1H), 3.47 (dd, *J* = 8.9, 6.2 Hz, 1H), 2.19 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 140.2, 139.4, 138.8, 129.8, 128.9, 128.7, 128.6, 128.3, 128.2, 127.9, 127.7, 127.5, 127.1, 125.4, 122.2, 121.6, 108.7, 82.1, 74.7, 74.3, 72.8, 71.8, 69.7, 69.1, 13.5; ESI-HRMS: m/z calcd for $C_{36}H_{37}NNaO_4$ [M + Na]$^+$: 570.2615; found: 570.2594.

**(2*R*,3*S*,4*R*)-1,3,4-tris(benzyloxy)-4-(1-(4-methoxyphenyl)-5-methyl-1*H*-pyrrol-3-yl)butan-2-ol (12o).** Obtained as a colorless syrup (45.0 mg, 78%); $[\alpha]_D^{25}$ -25.0 (*c* 0.32, EtOAc); $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.40–7.19 (m, 15H), 7.10–7.05 (m, 2H), 7.04 (s, 1H), 7.02 (s, 1H), 6.79 (d, *J* = 1.6 Hz, 1H), 6.08 (s, 1H), 4.56 (d, *J* = 6.1 Hz, 1H), 4.52 (m, 2H), 4.48 (d, *J* = 5.3 Hz, 2H), 4.35 (d, *J* = 7.0 Hz, 1H), 4.32 (d, *J* = 5.8 Hz, 1H), 4.24 (d, *J* = 10.9 Hz, 1H), 4.08 (br, 1H), 3.80 (s, 3H), 3.67 (d, *J* = 7.8 Hz, 1H), 3.53 (t, *J* = 7.9 Hz, 1H), 3.46 (t, *J* = 7.5 Hz, 1H), 2.14 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 158.4, 139.6, 139.4, 138.9, 133.2, 129.1, 128.6, 128.3, 127.9, 127.7, 127.5, 126.9, 121.8, 121.7, 114.8, 108.0, 82.1, 74.7, 74.3, 72.8, 71.8, 69.7, 69.1, 55.8, 13.3; ESI-HRMS: m/z calcd for $C_{37}H_{39}NNaO_5$ [M + Na]$^+$: 600.2720; found: 600.2728.

**(2*R*,3*S*,4*R*)-4-(1-([1,1'-biphenyl]-4-yl)-5-methyl-1*H*-pyrrol-3-yl)-1,3,4-tris(benzyloxy)butan-2-ol (12p).** Obtained as a colorless syrup (44.9 mg, 72%); $[\alpha]_D^{25}$ -14.0 (*c* 0.40, EtOAc); $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 7.7 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 3H), 7.38–7.33 (m, 9H), 7.28–7.22 (m, 4H), 7.12–7.02 (m, 2H), 6.93 (d, *J* = 1.6 Hz, 1H), 6.15 (s, 1H), 4.60 (d, *J* = 6.5 Hz, 1H), 4.57–4.46 (m, 4H), 4.37 (d, *J* = 7.4 Hz, 1H), 4.34 (d, *J* = 6.4 Hz, 1H), 4.25 (d, *J* = 10.8 Hz, 1H), 4.09 (br, 1H), 3.69 (dd, *J* = 7.9, 2.5 Hz, 1H), 3.59–3.50 (m, 1H), 3.47 (dd, *J* = 9.1, 6.0 Hz, 1H), 2.25 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 139.7, 139.6, 139.5, 139.4, 138.9, 138.8, 129.5, 128.7, 128.3, 128.1, 127.9, 127.6, 127.1, 125.8, 122.4, 121.6, 108.9, 82.1, 74.6, 74.3, 72.8, 71.8, 69.7, 69.1, 13.6; ESI-HRMS: m/z calcd for $C_{42}H_{41}NNaO_4$ [M + Na]$^+$: 646.2928; found: 646.2898.

**(2*R*,3*R*,4*R*)-4-(1-benzyl-5-methyl-1*H*-pyrrol-3-yl)-1,3,4-tris(benzyloxy)butan-2-ol (14a).** Obtained as a colorless syrup (41.7 mg, 74%); $[\alpha]_D^{25}$ -20.7 (*c* 0.29, EtOAc); $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.38–7.16 (m, 18H), 7.03 (d, *J* = 7.2 Hz, 2H), 6.72 (s, 1H), 5.87 (s, 1H), 5.07 (s, 2H), 4.81 (d, *J* = 4.8 Hz, 1H), 4.62 (s, 2H), 4.45 (d, *J* = 11.6 Hz, 2H), 4.42 (s, 2H), 4.30 (d, *J* = 12.0 Hz, 1H), 3.81–3.74 (br, 1H), 3.73–3.67(br, 1H), 3.57 (d, *J* = 9.1 Hz, 1H), 3.46 (t, *J* = 9.1 Hz, 1H), 2.07 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 139.8, 139.7, 139.4, 139.1, 129.0, 128.6, 128.5, 128.4, 127.5, 126.8, 120.7, 120.1, 106.7, 85.9, 76.7, 74.8, 72.6, 72.0, 70.4, 69.8, 49.9, 12.3; ESI-HRMS: m/z calcd for $C_{37}H_{39}NNaO_4$ [M + Na]$^+$: 584.2771; found: 584.2775.

**(2*R*,3*R*,4*R*)-1,3,4-tris(benzyloxy)-4-(1-butyl-5-methyl-1*H*-pyrrol-3-yl)butan-2-ol (14b).** Obtained as a colorless syrup (42.0 mg, 80%); $[\alpha]_D^{25}$ -33.8 (*c* 0.32, EtOAc); $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.38–7.18 (m, 15H), 6.57 (s, 1H), 5.77 (s, 1H), 4.77 (s, 1H), 4.61 (s, 2H), 4.47–4.36 (m, 4H), 4.26 (d, *J* = 11.7 Hz, 1H), 3.85–3.70 (m, 3H), 3.67 (s, 1H), 3.54 (s, 1H), 3.44 (s, 1H), 2.17 (s, 3H), 1.57 (s, 2H), 1.24 (d, *J* = 6.3 Hz, 2H), 0.86 (d, *J* = 6.3 Hz, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 139.9, 139.5, 139.1, 128.6, 128.5, 128.4, 127.9, 127.7, 127.5, 119.7, 119.5, 106.0, 86.0, 76.8, 74.7, 72.7, 72.0, 70.3, 69.7, 46.0, 33.3, 19.7, 14.0, 12.3; ESI-HRMS: m/z calcd for $C_{34}H_{41}NNaO_4$ [M + Na]$^+$: 550.2928; found: 550.2931.

**(2*R*,3*R*,4*R*)-1,3,4-tris(benzyloxy)-4-(1-cyclohexyl-5-methyl-1*H*-pyrrol-3-yl)butan-2-ol (14c).** Obtained as a colorless syrup (44.7 mg, 81%); $[\alpha]_D^{25}$ -20.5 (*c* 0.40, EtOAc); $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.41–7.18 (m, 15H), 6.64 (d, *J* = 1.5 Hz, 1H), 5.76 (s, 1H), 4.75 (d, *J* = 5.3 Hz, 1H), 4.66–4.55 (m, 2H), 4.45 (d, *J* = 6.4 Hz, 1H), 4.43–4.36 (m, 3H), 4.27 (d, *J* = 12.0 Hz, 1H), 3.81–3.69 (m, 2H), 3.66 (dd, *J* = 6.4, 4.2 Hz, 1H), 3.57 (dd, *J* = 10.0,

3.0 Hz, 1H), 3.43 (dd, *J* = 9.9, 6.8 Hz, 1H), 2.18 (s, 3H), 1.88–1.71 (m, 4H), 1.65 (d, *J* = 12.8 Hz, 1H), 1.50–1.31 (m, 4H), 1.21–1.15 (m, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 139.9, 139.8, 139.2, 128.6, 128.5, 128.4, 128.0, 127.9, 127.7, 127.5, 127.4, 119.7, 115.7, 105.6, 85.9, 77.0, 74.7, 72.6, 72.1, 70.3, 69.8, 54.5, 34.4, 34.2, 25.8, 25.5, 12.4; ESI-HRMS: m/z calcd for $C_{36}H_{43}NNaO_4$ [M + Na]$^+$: 576.3084; found: 576.3089.

**(1*R*,2*R*)-1-(1-benzyl-5-methyl-1*H*-pyrrol-3-yl)-1,3-bis(benzyloxy)propan-2-ol (16a).** Obtained as a colorless syrup (40.3 mg, 91%); $[\alpha]_D^{25}$ -35.2 (*c* 0.50, EtOAc); $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.44–7.13 (m, 13H), 7.00 (d, *J* = 6.9 Hz, 2H), 6.71 (s, 1H), 5.84 (s, 1H), 5.06 (s, 2H), 4.69 (s, 1H), 4.47 (d, *J* = 12.1 Hz, 1H), 4.42–4.34 (m, 2H), 4.30 (d, *J* = 12.1 Hz, 1H), 4.21 (d, *J* = 5.9 Hz, 1H), 3.85–3.75 (br, 1H), 3.45 (d, *J* = 9.1 Hz, 1H), 3.27 (t, *J* = 8.5 Hz, 1H), 2.06 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 139.6, 139.5, 139.1, 129.0, 128.7, 128.6, 128.5, 127.5, 126.8, 120.8, 120.0, 106.9, 77.0, 73.7, 72.7, 72.5, 69.4, 49.9, 12.2; ESI-HRMS: m/z calcd for $C_{29}H_{31}NNaO_3$ [M + Na]$^+$: 464.2196; found: 456.2198.

**(1*R*,2*R*)-1,3-bis(benzyloxy)-1-(1-butyl-5-methyl-1*H*-pyrrol-3-yl)propan-2-ol (16b).** Obtained as a colorless syrup (37.9 mg, 93%); $[\alpha]_D^{25}$ -48.3 (*c* 0.47, EtOAc); $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.42– 7.15 (m, 10H), 6.57 (s, 1H), 5.74 (s, 1H), 4.70–4.55 (br, 1H), 4.45-4.35 (m, 3H), 4.26 (d, *J* = 12.2 Hz, 1H), 4.16 (d, *J* = 6.7 Hz, 1H), 3.80–3.70 (m, 3H), 3.41 (dd, *J* = 9.9, 3.0 Hz, 1H), 3.22 (dd, *J* = 9.7, 6.3 Hz, 1H), 2.15 (s, 3H), 1.63–1.49 (m, 2H), 1.30–1.16 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 139.7, 139.1, 128.6, 128.5, 128.1, 127.9, 127.7, 127.5, 119.8, 119.3, 106.2, 77.0, 73.7, 72.6, 72.5, 69.3, 45.9, 33.3, 19.7, 14.0, 12.2; ESI-HRMS: m/z calcd for $C_{26}H_{33}NNaO_3$ [M + Na]$^+$: 430.2353; found: 430.2355.

**(1*R*,2*R*)-1,3-bis(benzyloxy)-1-(1-cyclohexyl-5-methyl-1*H*-pyrrol-3-yl)propan-2-ol (16c).** Obtained as a colorless syrup (38.9 mg, 90%); $[\alpha]_D^{25}$ -42.2 (*c* 0.50, EtOAc); $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.42–7.16 (m, 10H), 6.64 (d, *J* = 1.4 Hz, 1H), 5.73 (s, 1H), 4.61 (d, *J* = 4.9 Hz, 1H), 4.45–4.36 (m, 3H), 4.26 (d, *J* = 12.2 Hz, 1H), 4.19 (d, *J* = 6.5 Hz, 1H), 3.84–3.71 (m, 2H), 3.41 (d, *J* = 9.8 Hz, 1H), 3.22 (t, *J* = 8.3 Hz,1H), 2.16 (s, 3H), 1.90–1.74 (m, 4H), 1.66 (d, *J* = 12.4 Hz, 1H), 1.55–1.31 (m, 4H), 1.27–1.15 (m, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 139.7, 139.1, 128.8, 128.7, 128.6, 128.5, 128.0, 127.9, 127.8, 127.7, 127.5, 119.6, 115.8, 105.9, 77.1, 73.6, 72.6, 72.5, 69.4, 54.5, 34.3, 34.2, 25.9, 25.5, 12.4; ESI-HRMS: m/z calcd for $C_{28}H_{35}NNaO_3$ [M + Na]$^+$: 456.2509; found: 456.2513.

**(1*S*,2*R*)-1-(1-benzyl-5-methyl-1*H*-pyrrol-3-yl)-1,3-bis(benzyloxy)propan-2-ol (18a).** Obtained as a colorless syrup (39.3 mg, 89%); $[\alpha]_D^{25}$ +42.2 (*c* 0.50, EtOAc); $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.41–7.15 (m, 13H), 7.03 (d, *J* = 7.3 Hz, 2H), 6.70 (d, *J* = 1.5 Hz, 1H), 5.86 (s, 1H), 5.05 (s, 2H), 4.60 (d, *J* = 5.4 Hz, 1H), 4.50–4.41 (m, 3H), 4.30 (d, *J* = 12.1 Hz, 1H), 4.25 (d, *J* = 5.3 Hz, 1H), 3.92–3.82 (m, 1H), 3.57 (dd, *J* = 9.8, 3.6 Hz, 1H), 3.45 (dd, *J* = 9.8, 6.5 Hz, 1H), 2.06 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 139.6, 139.5, 139.2, 129.0, 128.6, 128.4, 128.0, 127.9, 127.7, 127.5, 126.9, 121.1, 119.6, 107.3, 77.3, 73.1, 72.7, 72.4, 69.6, 49.9, 12.3; ESI-HRMS: m/z calcd for $C_{29}H_{31}NNaO_3$ [M + Na]$^+$: 464.2196; found: 456.2200.

**(1*S*,2*R*)-1,3-bis(benzyloxy)-1-(1-butyl-5-methyl-1*H*-pyrrol-3-yl)propan-2-ol (18b).** Obtained as a colorless syrup (35.0 mg, 86%); $[\alpha]_D^{25}$ +55.3 (*c* 0.40, EtOAc); $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.40–7.17 (m, 10H), 6.56 (d, *J* = 1.5 Hz, 1H), 5.76 (s, 1H), 4.52 (d, *J* = 5.3 Hz, 1H), 4.46 (s, 2H), 4.42 (d, *J* = 12.1 Hz, 1H), 4.27 (d, *J* = 12.1 Hz, 1H), 4.21 (d, *J* = 5.4 Hz, 1H), 3.88–3.80 (m, 1H), 3.74 (t, *J* = 7.1 Hz, 2H), 3.55 (dd, *J* = 9.8, 3.5 Hz, 1H), 3.43 (dd, *J* = 9.8, 6.6 Hz, 1H), 2.15 (s, 3H), 1.65–1.53 (m, 2H), 1.33–1.19 (m, 3H), 0.89 (t, *J* = 7.4 Hz, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 139.7, 139.2, 128.6, 128.5, 128.0, 127.8, 127.7, 127.5, 120.0, 119.1, 106.6, 77.4, 73.2, 72.7, 72.4, 69.6, 45.9, 33.3, 19.8, 14.1, 12.3; ESI-HRMS: m/z calcd for $C_{26}H_{33}NNaO_3$ [M + Na]$^+$: 430.2353; found: 430.2354.

**(1*S*,2*R*)-1,3-bis(benzyloxy)-1-(1-cyclohexyl-5-methyl-1*H*-pyrrol-3-yl)propan-2-ol (18c).** Obtained as a colorless syrup (38.2 mg, 88%); $[\alpha]_D^{25}$ +45.7 (*c* 0.21, EtOAc); $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.39–7.20 (m, 10H), 6.63 (d, *J* = 1.3 Hz, 1H), 5.73 (s, 1H), 4.50 (d, *J* = 2.1 Hz, 1H), 4.46 (d, *J* = 1.0 Hz, 2H), 4.40 (d, *J* = 12.2 Hz, 1H), 4.26 (d, *J* = 12.2 Hz, 1H), 4.21 (d, *J* = 5.5 Hz, 1H), 3.86–3.80 (br, 1H), 3.80–3.71 (m, 1H), 3.60–3.53 (m, 1H), 3.47–3.39 (m, 1H), 2.16 (s, 3H), 1.93–1.73 (m, 4H), 1.66 (d, *J* = 12.3 Hz, 1H), 1.60–1.45 m, 2H), 1.45–1.32 (m, 2H), 1.23–1.15 (m, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 139.7, 139.2, 128.6, 128.5, 128.0, 127.8, 127.7, 127.5, 119.4, 116.0, 106.2, 77.7, 73.1, 72.7, 72.4, 69.6, 54.5, 34.3, 25.9, 25.5, 12.4; ESI-HRMS: m/z calcd for $C_{28}H_{35}NNaO_3$ [M + Na]$^+$: 456.2509; found: 456.2512.

**1-((1*S*,3*R*,4*S*,5*S*,6*S*)-4-(benzyloxy)-3-((benzyloxy)methyl)-2-oxabicyclo[3.1.0]hexan-6-yl)ethanone (17).** To a solution of (3a*S*,5*R*,6*R*,6a*S*)-6-(benzyloxy)-5-((benzyloxy)methyl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxole[22] (990.0 mg, 2.672 mmol) and allyltrimethylsilane (458.0 mg, 4.008 mmol) in $CH_2Cl_2$ (15 mL) at 0 °C, was dropwised $BF_3{\cdot}OEt_2$ (568.9 mg, 4.008 mmol). The reaction mixture was stirred at 0 °C for 1 hour and warmed to room temperature until the reaction was completed as detected by TLC. Then the reaction was quenched with a vigorously stirred solution of saturated aqueous $NaHCO_3$ (30 mL), and extracted with $CH_2Cl_2$ (3 × 20 mL). The organic layer was dried over $Na_2SO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (ethyl acetate/ petroleum ether = 1:15) to afford (2*R*,3*R*,4*S*,5*R*)-2-allyl-4-(benzyloxy)-5-((benzyloxy)methyl)tetrahydrofuran-3-ol as a colorless oil (640.1 mg, 67%). $[\alpha]_D^{25}$ +68.3 (*c* 0.40, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.36 (m, 10H), 5.98–5.77 (m, 1H), 5.13 (m, 2H), 4.66 (d, *J* = 11.8 Hz, 2H), 4.55 (dd, *J* = 11.8, 4.9 Hz, 2H), 4.26 (d, *J* = 2.5 Hz, 1H), 4.16–4.04 (m, 2H), 4.00 (s, 1H), 3.71 (dd, *J* = 10.3, 2.6 Hz, 1H), 3.60 (dd, *J* = 10.3, 2.4 Hz, 1H), 2.58–2.33 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 137.8, 137.2, 134.6, 128.6, 128.5, 128.1, 127.8, 127.6, 117.3, 87.4, 86.5, 82.7, 78.2, 73.9, 71.9, 71.2, 37.5; ESI-HRMS: m/z calcd for $C_{22}H_{26}NaO_4$ [M + Na]$^+$: 377.1723; found: 377.1724.

To a solution of (2*R*,3*R*,4*S*,5*R*)-2-allyl-4-(benzyloxy)-5-((benzyloxy)methyl)tetrahydrofuran-3-ol (640.1 mg, 1.806 mmol) in pyridine (5.0 mL) at 0 °C, was added TosCl (688.5 mg, 3.611 mmol). The reaction mixture was stirred at 50 °C until the reaction was completed as detected by TLC. Then the

reaction mixture was poured into a vigorously stirred solution of saturated aqueous NaCl (30 mL), and extracted with EtOAc (3 × 20 mL). The combined organic phases were dried over $Na_2SO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (ethyl acetate/ petroleum ether = 1:20) to afford (2*R*,3*R*,4*R*,5*R*)-2-allyl-4-(benzyloxy)-5-((benzyloxy)methyl)tetrahydrofuran-3-yl 4-methylbenzenesulfonate as a colorless oil (658.3 mg, 72%). $[\alpha]_D^{25}$ +54.5 (*c* 0.40, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.41–7.29 (m, 10H), 7.26–7.18 (m, 2H), 5.78–5.52 (m, 1H), 5.07 (s, 1H), 5.04 (d, *J* = 6.7 Hz, 1H), 4.84–4.75 (m, 1H), 4.54 (s, 2H), 4.44 (m, 2H), 4.15 (m, 3H), 3.53 (m, 2H), 2.45 (s, 3H), 2.37 (t, *J* = 6.9 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 145.2, 138.0, 137.4, 133.5, 133.3, 130.0, 128.4, 128.0, 127.9, 127.7, 118.1, 86.5, 84.8, 82.1, 81.9, 73.4, 72.0, 69.8, 36.3, 21.7; ESI-HRMS: m/z calcd for $C_{29}H_{32}NaO_6S$ $[M + Na]^+$: 531.1812; found: 531.1820.

To a suspension of (2*R*,3*R*,4*R*,5*R*)-2-allyl-4-(benzyloxy)-5-((benzyloxy)methyl)tetrahydrofuran-3-yl 4-methylbenzenesulfonate (658.3 mg, 1.294 mmol) and $Hg(OAc)_2$ (103.1 mg, 0.324 mmol) in acetone / $H_2O$ (V/V = 4:1, 15 mL) at 0 °C, was dropwised Jones reagent (2 N, 1.50 mL, 2.976 mmol). The reaction mixture was stirred at 0 °C for 1 hour and warmed to room temperature until the reaction was completed as detected by TLC. Then the reaction was quenched with *i*-PrOH (2.0 mL), and extracted with $CH_2Cl_2$ (3 × 20 mL). The organic layer was dried over $Na_2SO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (ethyl acetate/ petroleum ether = 1:5) to afford (2*R*,3*R*,4*R*,5*R*)-4-(benzyloxy)-5-((benzyloxy)methyl)-2-(2-oxopropyl)tetrahydrofuran-3-yl 4-methylbenzenesulfonate (420.9 mg, 62%). $[\alpha]_D^{25}$ +35.8 (*c* 0.40, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.40–7.29 (m, 10H), 7.24–7.13 (m, 2H), 4.89 (t, *J* = 2.7 Hz, 1H), 4.58–4.48 (m, 3H), 4.47–4.37 (m, 2H), 4.21–4.09 (m, 2H), 3.52 (m, 2H), 2.83 (dd, *J* = 16.6, 7.7 Hz, 1H), 2.74 (dd, *J* = 16.6, 5.5 Hz, 1H), 2.44 (s, 3H), 2.15 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 205.5, 145.2, 137.9, 137.2, 133.4, 130.0, 128.4, 128.0, 127.9, 127.7, 86.5, 84.2, 82.0, 78.5, 73.4, 72.1, 69.7, 45.6, 30.5, 21.7; ESI-HRMS: m/z calcd for $C_{29}H_{32}NaO_7S$ $[M + Na]^+$: 547.1761; found: 547.1763.

A mixture of (2*R*,3*R*,4*R*,5*R*)-4-(benzyloxy)-5-((benzyloxy)methyl)-2-(2-oxopropyl)tetrahydrofuran-3-yl 4-methylbenzenesulfonate (420.9 mg, 0.802 mmol) and $K_2CO_3$ (332.1 mg, 2.407 mmol) in DMSO (5.0 mL) was heated to 60 °C until the reaction was completed as detected by TLC. After the reaction was cooled to room temperature, it was poured into a vigorously stirred solution of saturated aqueous NaCl (30 mL), and extracted with EtOAc (3 × 20 mL). The organic layer was dried over $Na_2SO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (ethyl acetate/ petroleum ether = 1:6) to afford product 17 as a colorless syrup (192.2 mg, 68%).$[\alpha]_D^{25}$ +146.7 (*c* 0.30, EtOAc); $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.39–7.26 (m, 10H), 4.62–4.42 (m, 4H), 4.35 (t, *J* = 5.6 Hz, 1H), 4.17 (d, *J* = 5.2 Hz, 1H), 3.73 (d, *J* = 3.8 Hz, 1H), 3.52–3.42 (m, 2H), 2.71 (d, *J* = 3.2 Hz, 1H), 2.40 (dd, *J* = 9.1, 4.7 Hz, 1H), 2.17 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 204.2, 138.6, 128.7, 128.2, 128.0, 127.9, 82.2, 80.3, 72.7, 71.3, 70.0, 68.3, 31.4, 30.8, 30.1; ESI-HRMS: m/z calcd for $C_{22}H_{24}NaO_4$ $[M + Na]^+$: 375.1567; found: 375.1571**.**

**(2*S*,3*S*,4*R*)-1,3,4-tris(benzyloxy)-4-(5-methyl-1-phenyl-1*H*-pyrrol-3-yl)butan-2-ol (19).** To a solution of alcohol **12n** (100 mg, 0.183 mmol) and pyridine (43.3 mg, 0.548 mmol) in $CH_2Cl_2$ (4.0 mL) at -10 °C, was dropwise $Tf_2O$ (103.0 mg, 0.365 mmol). The reaction mixture was stirred at -10 °C until the reaction was completed as detected by TLC. Then the reaction was quenched with a vigorously stirred solution of saturated aqueous $NaHCO_3$ (5 mL), and extracted with $CH_2Cl_2$ (3 × 5 mL). The organic layer was dried over $Na_2SO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (ethyl acetate/ petroleum ether = 1:20) to afford crude triflate (76.2 mg).

To a solution of the crude triflate (76.2 mg) in DMF (2.0 mL) at room temperature was added $NaNO_2$ (25.2 mg, 0.365 mmol). After the reaction mixture was stirred for 12 hours, a solution of saturated aqueous NaCl (10 mL) was added. Then the mixture was extracted with EtOAc (3 × 10 mL). The organic layer was dried over $Na_2SO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (ethyl acetate/ petroleum ether = 1:15) to afford pyrrole **19** as a colorless syrup (26 mg, 26%); $[\alpha]_D^{25}$ -18.7 (*c* 0.60, EtOAc); $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.54–7.46 (m, 2H), 7.41–7.30 (m, 11H), 7.27 (m, 5H), 7.22–7.16 (m, 2H), 6.85 (d, *J* = 1.8 Hz, 1H), 6.08 (s, 1H), 4.94 (d, *J* = 5.8 Hz, 1H), 4.74 (d, *J* = 11.3 Hz, 1H), 4.65 (d, *J* = 4.3 Hz, 1H), 4.61 (d, *J* = 11.4 Hz, 1H), 4.54 (d, *J* = 12.1 Hz, 1H), 4.46 (s, 2H), 4.34 (d, *J* = 12.1 Hz, 1H), 3.80 (dd, *J* = 6.7, 4.3 Hz, 1H), 3.72–3.65 (m, 1H), 3.60 (dd, *J* = 9.9, 2.4 Hz, 1H), 3.48 (dd, *J* = 9.9, 6.4 Hz, 1H), 2.18 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 140.3, 139.6, 139.1, 129.8, 128.6, 128.5, 128.4, 128.1, 128.0, 127.8, 127.7, 127.6, 127.0, 125.3, 121.3, 120.7, 109.5, 83.2, 76.9, 74.2, 72.8, 72.6, 70.3, 69.9, 13.5; ESI-HRMS: m/z calcd for $C_{36}H_{37}NNaO_4$ $[M + Na]^+$: 570.2615; found: 570.2614.

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