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Paper

Arkivoc **2020**, part vi, 0-0

Bioinspired stereoselective synthesis of chiral 2,5-diaryl-3,4-dimethyltetrahydrofurans from unprotected 1,4-diarylbutane-1,4-diols

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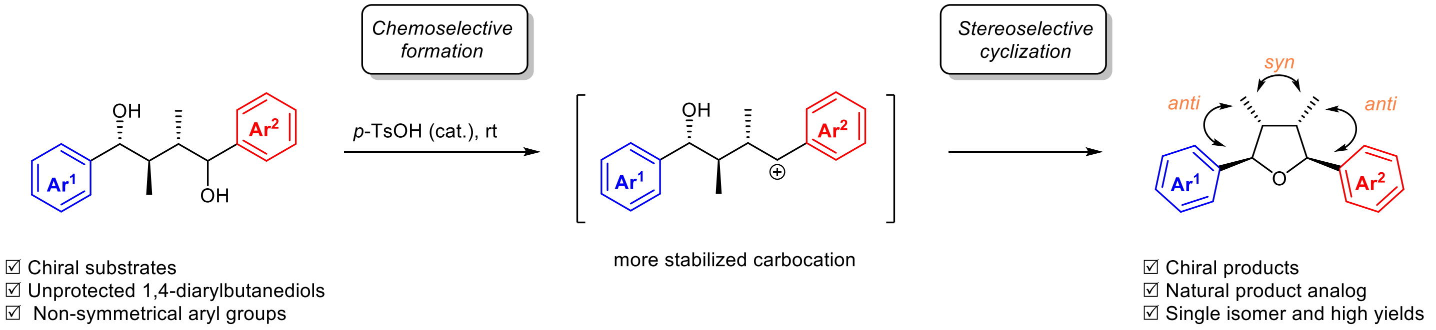
Received 06-19-2020 **Accepted** 08-06-2020 **Published on line** 08-25-2020

Abstract

A bioinspired stereoselective synthesis of (2,3-*anti*-3,4-*syn*-4,5-*anti*)-2,5-diaryl-3,4-dimethyltetrahydrofurans from unprotected chiral 1,4-diarylbutane-1,4-diols is described. Upon treatment of the chiral 1,4-diarylbutane-1,4-diols with acid, chiral 2,5-diaryl-3,4-dimethyltetrahydrofurans were obtained in high yields and high stereoselectivity through the chemoselective formation of a more stabilized benzylic carbocation followed by a stereoselective cyclization. Proposedly, the carbocation formation was chemoselectively governed by the substitution patterns of the non-symmetrical aryl groups of the 1,4-diarylbutane-1,4-diols and the stereoselective cyclization of the carbocation was inherently controlled by the stereochemistry of the substrates. The present study highlights a practical and an atom-economic process and provides essential information applicable for further design of the asymmetric synthesis of naturally occurring 2,5-diaryl-3,4-dimethyltetrahydrofurans and their derivatives isolated from *Krameria cystisoides*.



☑ Chiral substrates
☑ Unprotected 1,4-diarylbutanediols
☑ Non-symmetrical aryl groups

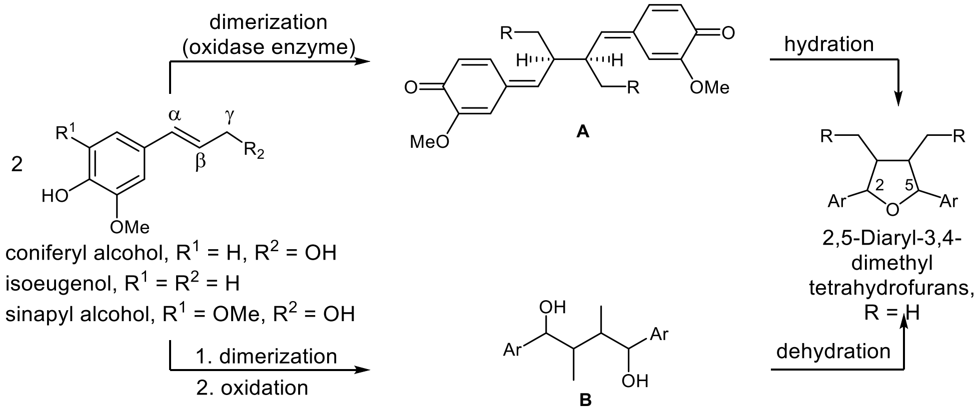
☑ Chiral products
☑ Natural product analog
☑ Single isomer and high yields

Keywords: Natural products, lignans, 2,5-diaryl-3,4-dimethyltetrahydrofurans, asymmetric synthesis

DOI: https://doi.org/10.24820/ark.5550190.p011.276

Introduction

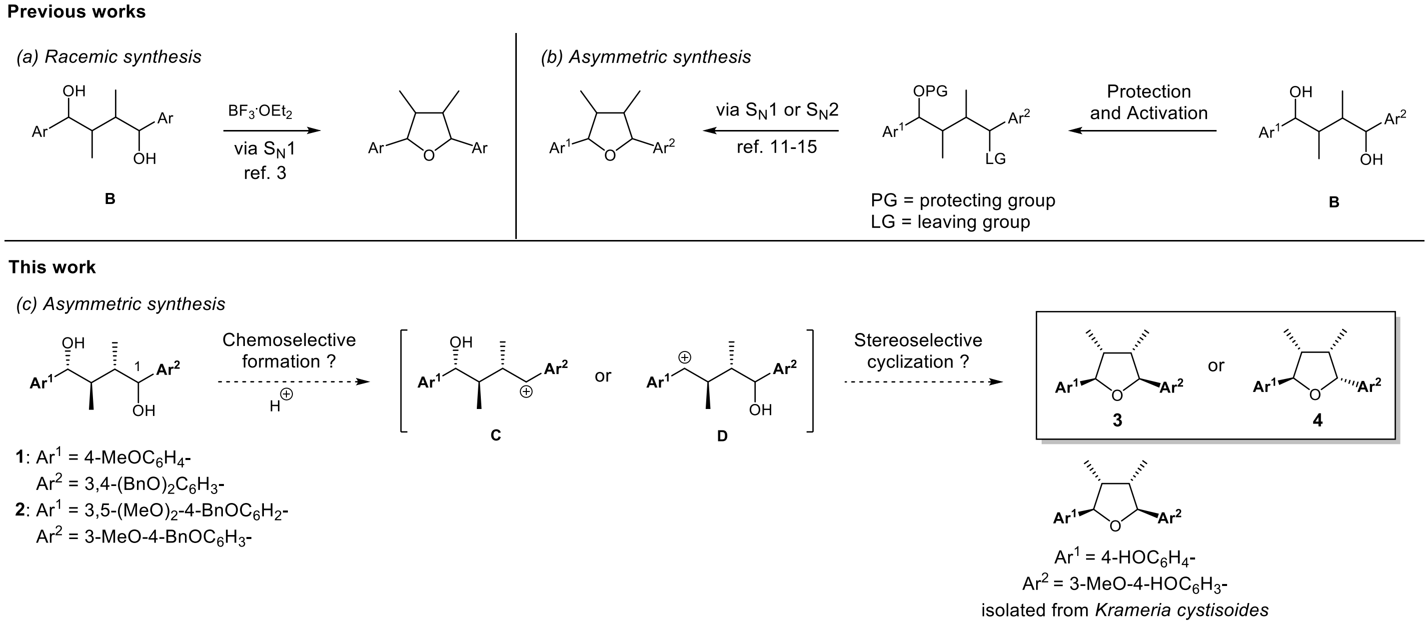
The development of synthetic methodologies to access enantioenriched 2,5-diaryl-3,4-dimethyltetrahydrofurans which are important members of classical lignans remains highly important in the organic synthesis community. Among the developed methods, the syntheses based on bioinspired processes received considerable attention.[1-5] Biosynthetically, 2,5-diaryl-3,4-dimethyltetrahydrofurans are proposed to be derived from the oxidative dimerization of two C6–C3 units, such as coniferyl alcohol or isoeugenol, with a β-β′ linkage pattern to form a quinone methide intermediate **A** followed by hydration (Scheme 1). Alternatively, biosynthetic pathway *via* dimerization of C6–C3 units, such as sinapyl alcohol, followed by oxidation and dehydration of 1,4-diarylbutane diols **B** was also proposed.[6-8] Based on the latter biosynthetic pathway, a number of reports on the synthesis of 2,5-diaryl-3,4-dimethyltetrahydrofurans, both racemic and chiral forms, employing **B** as key advanced intermediates have been complied.[9,10]



Scheme 1. Proposed biosynthetic pathways of 2,5-diaryl-3,4-dimethyltetrahydrofurans.

In general, a racemic synthesis of 2,5-diaryl-3,4-dimethyltetrahydrofurans from 1,4-diarylbutane-1,4-diols **B** bearing two symmetrical aromatic (Ar) groups could be readily achieved *via* Lewis acid-mediated cyclization (Scheme 2a).[3] On the contrary, to access chiral 2,5-diaryl-3,4-dimethyltetrahydrofurans, asymmetric transformation of chiral 1,4-diarylbutane-1,4-diols **B**, especially those containing non-symmetrical Ar rings, is highly challenging from both chemo- and stereoselectivity points of view. Thus, the synthesis of chiral 2,5-diaryl-3,4-dimethyltetrahydrofurans bearing two different aryl groups usually required selective protection and activation of the two unidentical hydroxy groups (Scheme 2b).[11-15] With an atom-economy concern, a synthetic strategy that allows simple and direct transformation of chiral 1,4-diarylbutane-1,4-diols **B** to chiral 2,5-diaryl-3,4-dimethyltetrahydrofurans in a chemo- and stereoselective manner is highly desirable and deserves investigation.[16,17]

Having been interested on the synthetic approach to access chiral 2,5-diaryl-3,4-dimethyltetrahydrofurans bearing 2,3-*anti*-3,4-*syn*-4,5-*anti* relative stereochemistry,[18-21] we primarily investigated an acid-catalyzed reaction of chiral 1,4-diarylbutane-1,4-diols **1** and **2**. The results from this work would provide an insight on the factors that govern chemoselective formation of carbocations followed by their stereoselective cyclization reactions to chiral 1,4-diarylbutane-1,4-diols **1** and **2** (Scheme 2c). Therefore, the chiral 1,4-diarylbutane-1,4-diols **1** and **2** bearing two different aryl groups (Ar^1 and Ar^2) where each has a different number of electron donating groups (EDGs) were designed and synthesized. On the basis that electron-rich Ar assisting carbocation formation, acid-catalyzed reaction of **1** should preferably lead to a carbocation intermediate **C** while **2** should give **D**. Additionally, two diastereoisomers for each of **1** and **2** were also designed and prepared for a detailed study on both chemo- and stereoselectivity of these reactions. In the cyclization step, the stereoselectivity of cyclization should be controlled by the steric effect resulting from the inherent stereochemistry of the two adjacent methyl groups. Thus, **C** would readily undergo cyclization leading to **3** as a single product while **D** should give a mixture of **3** and **4**, respectively. The application of the present study to synthesize a natural product derivative and the confirmation of the absolute configurations of 2,5-diaryl-3,4-dimethyltetrahydrofurans isolated from *Krameria cystisoides* were demonstrated.[18,19]

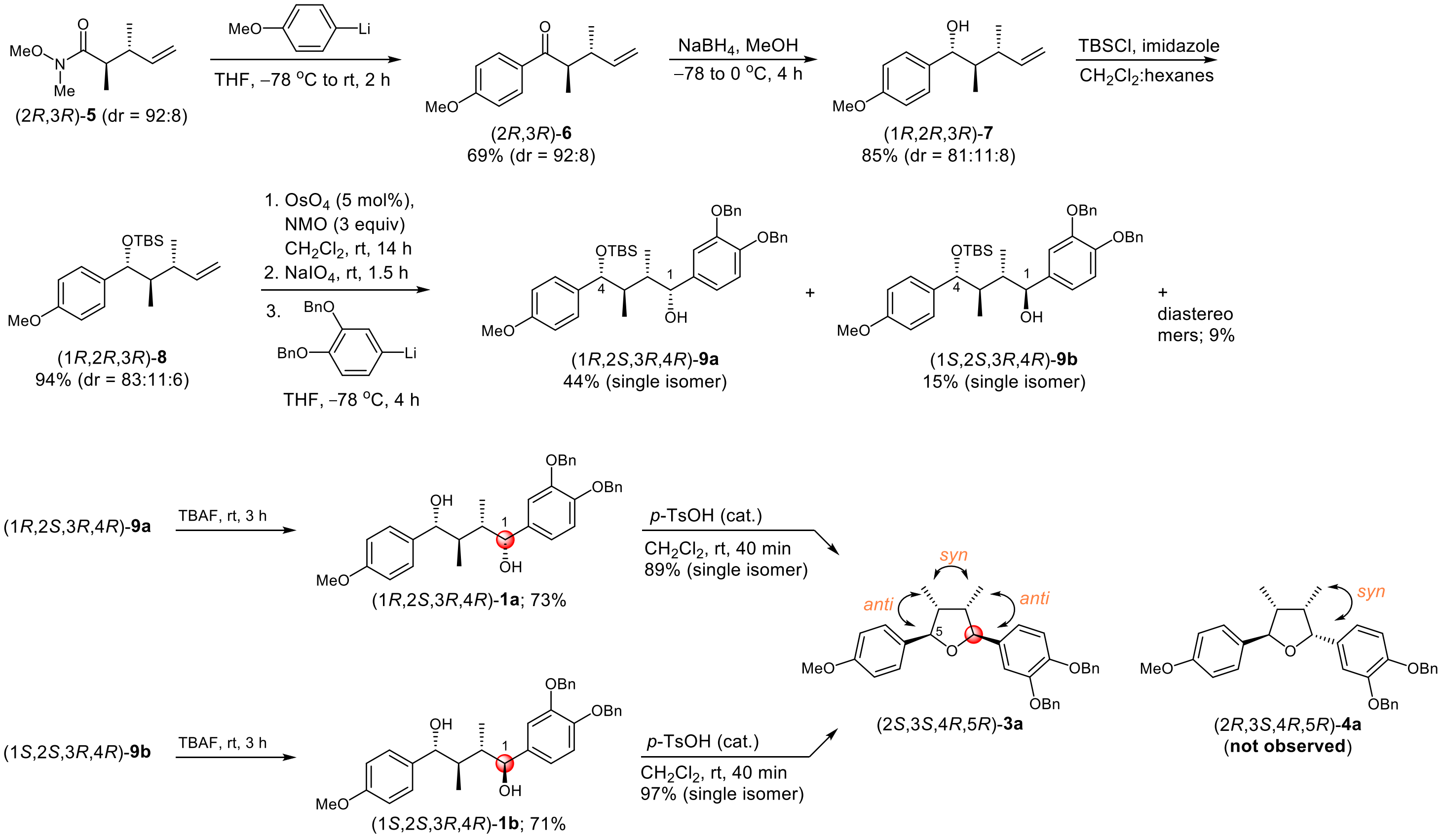


Scheme 2. Synthesis of 2,5-diaryl-3,4-dimethyltetrahydrofurans from 1,4-diarylbutane-1,4-diols.

Results and Discussion

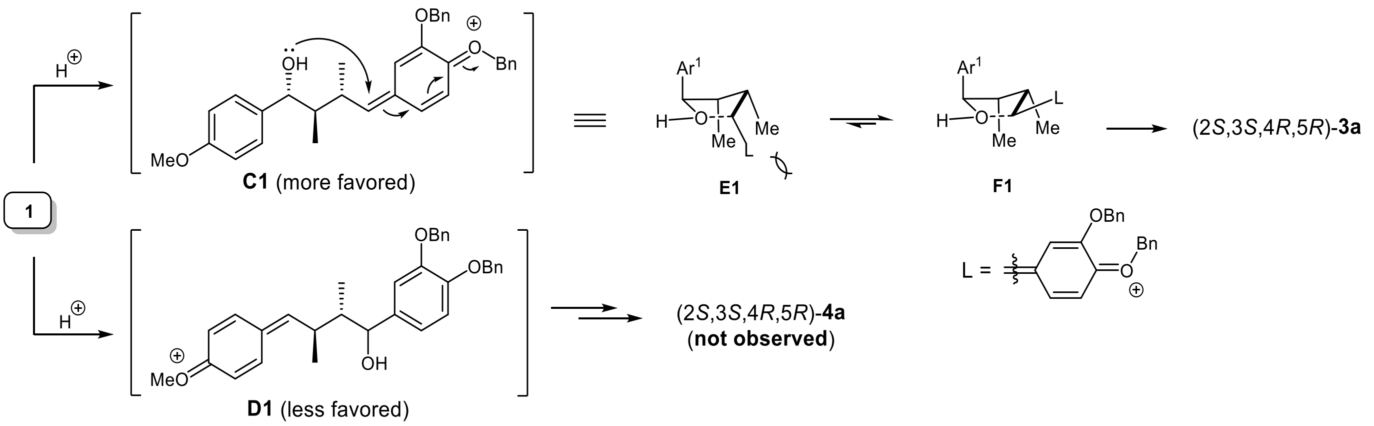
The chiral 1,4-diarylbutane-1,4-diol **1** (Ar^1/Ar^2 = mono-/di-EDGs) was first prepared (Scheme 3). The reaction of Weinreb amide (2*R*,3*R*)-**5** (dr = 92:8)[16] with 4-methoxyphenyllithium, freshly prepared from Li/Br exchange reaction between 4-bromo-1-methoxybenzene and *n*-BuLi, gave the corresponding (2*R*,3*R*)-ketone **6** in 69% yield (dr = 92:8). Ketone (2*R*,3*R*)-**6** was then treated with $NaBH_4$ in MeOH at –78 to 0 °C to provide the (1*R*,2*R*,3*R*)-alcohol **7** (85% yield) as an inseparable diastereomeric mixture (dr = 81:11:8, ^1H NMR analysis). Similar results were observed when DIBAL-H was employed as a reducing agent in THF at −78 °C. The stereochemical outcome of the hydride reduction to give (1*R*,2*R*,3*R*)-**7** as a major diastereomer could be explained on the basis of the Felkin–Anh model; the coupling constants ($^3J_{H1,2}$) of (1*R*,2*R*,3*R*)-**7** and two diastereomers are 9.3, 6.4, and 9.0 Hz, respectively (see the Supplementary Material). Protection of a hydroxy group of (1*R*,2*R*,3*R*)-**7** gave the TBS-ether (1*R*,2*R*,3*R*)-**8** in 94% yield; with a dr = 83:11:6. Next, an oxidative cleavage of the alkene moiety of (1*R*,2*R*,3*R*)-**8** followed by treatment of the obtained aldehyde with freshly prepared [3,4-bis(benzyloxy)phenyl]lithium provided (1*R*,2*S*,3*R*,4*R*)-**9a** (44% yield) and (1*S*,2*S*,3*R*,4*R*)-**9b** (15% yield), each as a single diastereomer, together with their diastereomers (9% yield). The relative stereochemistry of (1*R*,2*S*,3*R*,4*R*)-**9a** and (1*S*,2*S*,3*R*,4*R*)-**9b** was assigned by the analysis of the coupling constants between H-1/H-2 and H-3/H-4 (for (1*R*,2*S*,3*R*,4*R*)-**9a**; $^3J_{H1,2}$ = 4.6 Hz, $^3J_{H3,4}$ = 6.8 Hz, for (1*S*,2*S*,3*R*,4*R*)-**9b**; $^3J_{H1,2}$ = 7.8 Hz, $^3J_{H3,4}$ = 9.8 Hz, see the Supplementary Material). TBS deprotection of (1*R*,2*S*,3*R*,4*R*)-**9a** and

(1*S*,2*S*,3*R*,4*R*)-**9b** using TBAF in THF gave (1*R*,2*S*,3*R*,4*R*)-**1a** and (1*S*,2*S*,3*R*,4*R*)-**1b**, in 73% and 71% yields, respectively (for (1*R*,2*S*,3*R*,4*R*)-**1a**; $^3J_{H1,2}$ = 0 Hz, $^3J_{H3,4}$ = 9.6 Hz, for (1*S*,2*S*,3*R*,4*R*)-**1b**; H-1 and H-4 are overlapped and appear as multiplets).



Scheme 3. The synthesis and the direct cyclization of (1*R*,2*S*,3*R*,4*R*)-**1a** and (1*S*,2*S*,3*R*,4*R*)-**1b**.

To begin with, an acid-catalyzed cyclization reaction of (1*R*,2*S*,3*R*,4*R*)-**1a** and (1*S*,2*S*,3*R*,4*R*)-**1b** was investigated. Proposedly, upon treatment of (1*R*,2*S*,3*R*,4*R*)-**1a** and (1*S*,2*S*,3*R*,4*R*)-**1b** with an acid, a benzylic carbocation of type **C** would be chemoselectively generated due to a greater ability of Ar^2 bearing two EDGs versus Ar^1 to stabilize the carbocation (Scheme 2c). Indeed, when (1*R*,2*S*,3*R*,4*R*)-**1a** was simply treated with a catalytic amount of *p*-TsOH monohydrate in CH_2Cl_2 at room temperature, (2*S*,3*S*,4*R*,5*R*)-**3a** bearing 2,3-*anti*-3,4-*syn*-4,5-*anti* relative stereochemistry was obtained in 89% yield as a single diastereomer. The relative stereochemistry at the 2,3 and 3,4-positions were assigned by analysis of the coupling constants between H-2/H-3 and H-4/H-5; H-2 and H-5 each appeared as a doublet at δ 4.43 (d, $^3J_{H2,3}$ = 7.2 Hz) and δ 4.41 (d, $^3J_{H4,5}$ = 6.8 Hz) ppm, respectively. The NOESY experiments supported the assigned relative stereochemistry of (2*S*,3*S*,4*R*,5*R*)-**3a** (see the Supplementary Material). The formation of (2*S*,3*S*,4*R*,5*R*)-**3a** from (1*R*,2*S*,3*R*,4*R*)-**1a** implied that the benzylic carbocation **C1** (**C1** vs. **D1**) was chemoselectively generated and underwent stereoselective cyclization through a more favorable intermediate **F1** (**E1** vs. **F1**) affording (2*S*,3*S*,4*R*,5*R*)-**3a** in good yield with high stereoselectivity (Scheme 4). Under similar reaction conditions, (1*S*,2*S*,3*R*,4*R*)-**1b** was readily converted to (2*S*,3*S*,4*R*,5*R*)-**3a** as a single isomer in 97% yield (Scheme 3). This observation confirmed that the synthetic process proceeded through chemoselective formation of **C1** followed by stereoselective cyclization. It should be noted that (2*R*,3*S*,4*R*,5*R*)-**4a** possessing the 2,3-*syn*-3,4-*syn*-4,5-*anti* relative stereochemistry derived from either formation of carbocation **D1** or non-stereoselective cyclization of **C1** was not detected in the crude mixture (^{1}H-NMR analysis).

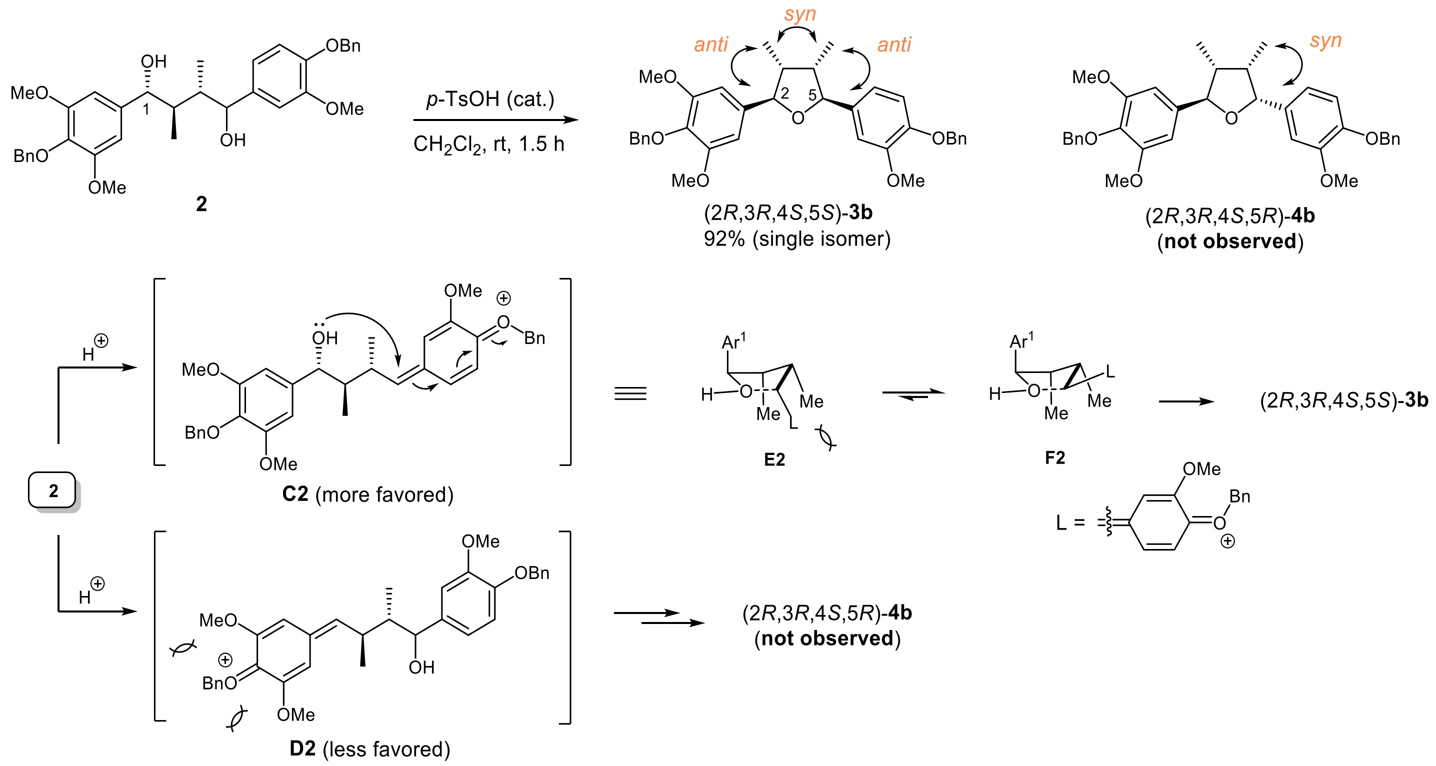


Scheme 4. Proposed mechanism for the formation of (2*S*,3*S*,4*R*,5*R*)-**3a**.

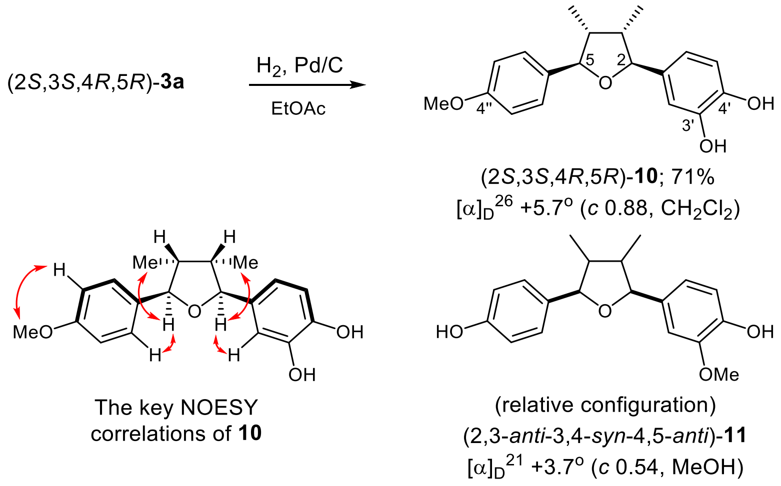
Encouraged by the above results, a racemic mixture of **2** (Ar^1/Ar^2 = tri-/di-EDGs) was prepared and subjected to an acid-catalyzed reaction. On the same basis, it is expected that **2** should give a benzylic carbocation of type **D** (Scheme 2c) due to a greater ability of Ar^1 having three EDGs (Ar^1 vs. Ar^2) to stabilize a carbocation intermediate **D**. Consecutive cyclization of **D** should give a mixture of **3** and **4**. Experimentally, upon treatment of **2** with *p*-TsOH monohydrate in CH_2Cl_2 at room temperature, (2*R*,3*R*,4*S*,5*S*)-**3b** bearing the 2,3-*anti*-3,4-*syn*-4,5-*anti* relative stereochemistry was obtained in 92% yield as a single diastereomer[16] while (2*R*,3*R*,4*S*,5*R*)-**4b** was not detected (Scheme 5). The results obtained implied that the carbocation intermediate **C2** instead of **D2** was chemoselectively generated from **2** and underwent stereoselective cyclization to give (2*R*,3*R*,4*S*,5*S*)-**3b**. This presumably dues to the developing steric interaction between the adjacent methoxy and benzyloxy substituents on the aromatic ring of carbocation intermediate **D2**. The destabilization effect of MeO group located on the meta positions with respect to the forming carbocation **D2** should not be excluded.

The study on the acid-catalyzed direct cyclization of **1** and **2** provided the information that the substitution patterns and types of the substituents on the aromatic rings of **1** and **2** were highly important for chemoselective formation of the benzylic carbocation in the first step. Not only an electronic nature but also the steric effect causing by the substituents on the aryl rings plays an important role. In the cyclization process, the inherent stereochemistry presenting in **1** and **2** dictated the stereoselectivity of the reaction providing (2*S*,3*S*,4*R*,5*R*)-**3a** and (2*R*,3*R*,4*S*,5*S*)-**3b** in good yields and high stereoselectivity.

Finally, (2*S*,3*S*,4*R*,5*R*)-**3a** was subjected to hydrogenolysis (H_2, Pd/C, EtOAc) to provide (2*S*,3*S*,4*R*,5*R*)-**10** in 71% yield as a single isomer (Scheme 6). The spectroscopic data of (2*S*,3*S*,4*R*,5*R*)-**10** {$[\alpha]_D^{26}$ +5.7 (*c* 0.88, CH_2Cl_2)} are almost identical to those reported for (2,3-*anti*-3,4-*syn*-4,5-*anti*)-5-(4-hydroxyphenyl)-2-(4-hydroxy-3-methoxyphenyl)-3,4-dimethyltetrahydrofuran (**11**) {$[\alpha]_D^{21}$ +3.7 (*c* 0.54, MeOH)}[18] isolated from *Krameria cystisoides* (see the Supplementary Material). Thus, the (2*S*,3*S*,4*R*,5*R*) absolute configurations presenting in the tetrahydrofuran-core of **11** was then confirmed.



Scheme 5. Acid-catalyzed a direct cyclization of **2**.



Scheme 6. Synthesis of (2*S*,3*S*,4*R*,5*R*)-**10**.

Table 1. The spectroscopic data of (2*S*,3*S*,4*R*,5*R*)-**10** and natural compound **11**[18]

position	(2,3-*anti*-3,4-*syn*-4,5-*anti*)-**11**[a]		(2*S*,3*S*,4*R*,5*R*)-**10**[a]	
	δ_H[b]	δ_C[c]	δ_H[d,f]	δ_C[e,f]
2	4.40 (br d, 6.7)	88.17*	4.34 (d, 6.4)	88.16
3	2.25 (m)	45.35†	2.26-2.16 (m)	45.73†
4	2.25 (m)	45.65†	2.26-2.16 (m)	45.77†
5	4.40 (br d, 6.7)	87.95*	4.40 (d, 6.5)	87.83
3-Me	0.95-1.05 (m)	12.95‡	0.99 (d, 5.2)	13.05‡
4-Me	0.95-1.05 (m)	13.12‡	0.99 (d, 5.2)	13.15‡
1′	-	135.28	-	135.50
2′	7.06 (d, 1.5)	111.03	7.00 (br s)	114.41
3′	-	148.30	-	145.94
4′	-	146.89	-	145.39
5′	7.32 (dm, 8.5)	115.48	6.79 (br s)	115.84
6′	7.32 (dm, 8.5)	119.95	6.79 (br s)	118.88
1″	-	134.44	-	135.76
2″ and 6″	6.69-6.98 (m)	128.53	7.39 (d, 8.5)	128.49
3″ and 5″	6.69-6.98 (m)	115.91	6.92 (d, 8.5)	114.55
4″	-	157.71	-	160.20
-OMe	3.85 (s)	56.35	3.79 (s)	55.59
-OH	-	-	7.82* (br s)	-
-OH	-	-	7.79* (br s)	-

[a]Data were measured in acetone-d_6. [b]δ_H (mult., *J* in Hz) (90 MHz). [c]δ_C (22.5 MHz). [d]δ_H (mult., *J* in Hz) (400 MHz). [e]δ_C (100 MHz). [f]Unless stated otherwise, the assignment was confirmed on the basis of HSQC and HMBC correlations. *, †, ‡ Similar values within a column may be interchanged.

Conclusions

In conclusion, the investigation on a direct cyclization of unprotected chiral 1,4-diarylbutane-1,4-diols to access unsymmetrical chiral 2,5-diaryl-3,4-dimethyltetrahydrofurans bearing the 2,3-*anti*-3,4-*syn*-4,5-*anti* relative stereochemistry is reported. Upon treatment with an acid, chiral 1,4-diarylbutane-1,4-diols underwent chemoselective formation of a more stabilized benzylic carbocation followed by stereoselective cyclization leading to chiral furan products in high yields and stereoselectivity in a single operation. Chemoselective generation of the carbocation intermediate was proposed to be governed by the electronic nature and the steric effect of the substituents on the aromatic rings of 1,4-diarylbutane-1,4-diols while stereoselective cyclization of the carbocation was presumably controlled by the inherent stereochemistry of the substrates. The present study represents a practical and an atom-economic process providing useful information applicable for further design asymmetric synthesis of bioactive 2,5-diaryl-3,4-dimethyltetrahydrofurans.

Experimental Section

General. The ^{1}H NMR spectra were recorded on a Bruker-400 (400 MHz) spectrometer in acetone-*d*$_6$ or CDCl$_3$ using tetramethylsilane as an internal standard. The ^{13}C NMR spectra were recorded on either a Bruker-400 (100 MHz) or JNM-ECZS (100 MHz) spectrometer in acetone-*d*$_6$ or CDCl$_3$ using residual non-deuterated solvent peaks as an internal standard. Tetrahydrofuran (THF) was distilled from sodium-benzophenone ketyl. Dichloromethane (CH_2Cl_2) and ethyl acetate (EtOAc) were distilled over calcium hydride and stored over activated molecular sieves (4 Å). Methanol (MeOH) was distilled over Mg powder. Other common solvents (CH_2Cl_2, hexanes, and EtOAc) were distilled before use. All glassware including needles and syringes were oven-dried and kept in a desiccator before use. Purification was carried out by column chromatography on silica gel. Weinreb amide (2*R*,3*R*)-**5** and compound **2** were synthesized according to the literature procedure. The spectroscopic data of (2*R*,3*R*,4*S*,5*S*)-**3b** are in agreement with those reported.[16]

(2*R*,3*R*)-1-(4-Methoxyphenyl)-2,3-dimethylpent-4-en-1-one [(2*R*,3*R*)-6]. A flame-dried round bottom flask equipped with a magnetic stirring bar, an argon inlet, and a rubber septum was charged with 4-bromo-1-methoxybenzene (398.7 mg, 2.13 mmol) and dry THF (5 mL). The solution was cooled at −78 °C then a solution of *n*-BuLi (1.6 M in hexanes, 1.3 mL, 2.08 mmol) was added dropwise. After stirring for 10 min, a solution of Weinreb amide (2*R*,3*R*)-**5** (280 mg, 1.64 mmol) in dry THF (5 mL) was added dropwise at −78 °C. The reaction mixture was stirred and slowly warmed up to room temperature. After stirring at room temperature for 2 h, the reaction mixture was quenched with H_2O (15 mL) and extracted with EtOAc (3 × 25 mL). The combined organic phase was washed with brine (20 mL), dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. Purification by column chromatography (EtOAc:hexanes, 1:9 v/v) afforded (2*R*,3*R*)-**6** (245.3 mg, 69% yield) with a 92:8 diastereomeric ratio; a colorless oil. R$_f$ 0.45 (EtOAc:hexanes, 1:9 v/v); $[\alpha]_D^{23}$ −39.8 (*c* 1.43, CHCl$_3$). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.95 (d, *J* 8.8 Hz, 2H, Ar*H*), 6.94 (d, *J* 8.8 Hz, 2H, Ar*H*), 5.75–5.64 (m, 1H, C*H*), 5.06–4.98 (m, 2H, C*HH*), 3.87 (s, 3H, OC*H*$_3$), 3.35–3.25 (m, 1H, C*H*), 2.68–2.54 (m, 1H, C*H*), 1.11 (d, *J* 6.8 Hz, 3H, C*H*$_3$), 0.99 (d, *J* 6.7 Hz, 3H, C*H*$_3$). ^{13}C NMR (100 MHz, CDCl$_3$): δ 203.0 (CO), 163.6 (C), 141.5 (CH), 130.7 (2 × CH), 130.5 (C), 115.1 (CH$_2$), 113.9 (2 × CH), 55.6 (OCH$_3$), 45.3 (CH), 41.3 (CH), 19.2 (CH$_3$), 15.9 (CH$_3$). IR (ATR): ν_{max} 1669s, 1597s, 1509m, 1457m, 1253s, 1172s cm^{-1}. MS: *m/z* (%) relative intensity 219 [(M + H)$^+$, 60], 218 (M$^+$, 24), 204 (2), 136 (16), 135 (31). HRMS (ESI-TOF) calcd for $C_{14}H_{18}O_2Na$ [M + Na]$^+$: 241.1204, found: 241.1206.

(1*R*,2*R*,3*R*)-1-(4-Methoxyphenyl)-2,3-dimethylpent-4-en-1-ol [(1*R*,2*R*,3*R*)-7]. A flame-dried round bottom flask equipped with a magnetic stirring bar, an argon inlet, and a rubber septum was charged with (2*R*,3*R*)-**6** (231.9 mg, 1.06 mmol) and dry MeOH (8 mL). The solution was cooled at −78 °C and NaBH$_4$ (160.4 mg, 4.25 mmol) was added. The reaction mixture was slowly warmed up to 0 °C over 3 h and the stirring was continued at 0 °C for 1 h. Then it was quenched with H_2O (10 mL) and extracted with EtOAc (3 × 15 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. Purification by column chromatography (EtOAc:hexanes, 1:4 v/v) provided (1*R*,2*R*,3*R*)-**7** (199.2 mg, 85% yield) with a 81:11:8 diastereomeric ratio; a colorless oil. R$_f$ 0.52 (EtOAc:hexanes, 1:4 v/v); $[\alpha]_D^{24}$ +6.8 (*c* 2.21, CHCl$_3$). ^{1}H

NMR (400 MHz, $CDCl_3$): δ 7.23 (d, *J* 8.6 Hz, 2H, Ar*H*), 6.87 (d, *J* 8.6 Hz, 2H, Ar*H*), 5.93–5.81 (m, 1H, C*H*), 5.16–5.06 (m, 2H, C*HH*), 4.32 (d, *J* 9.3 Hz, 1H, C*H*), 3.81 (s, 3H, OC*H*$_3$), 2.89–2.78 (m, 1H, C*H*), 1.87–1.77 (m, 1H, C*H*), 1.08 (d, *J* 7.0 Hz, 3H, C*H*$_3$), 0.55 (d, *J* 7.0 Hz, 3H, C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2 (C), 140.9 (CH), 136.4 (C), 128.2 (2 × CH), 115.1 (CH_2), 113.9 (2 × CH), 77.1 (CH), 55.4 (OCH_3), 45.3 (CH), 37.6 (CH), 18.6 (CH_3), 11.2 (CH_3). IR (ATR): ν_{max} 3431br, 1611m, 1511s, 1458m, 1246s, 1174s cm^{-1}. MS: *m/z* (%) relative intensity 220 (M$^+$, 7), 203 (100). HRMS (ESI-TOF) calcd for $C_{14}H_{20}O_2Na$ [M + Na]$^+$: 243.1361, found: 243.1359.

***tert*-Butyl{[(1*R*,2*R*,3*R*)-1-(4-methoxyphenyl)-2,3-dimethylpent-4-en-1-yl]oxy}dimethylsilane [(1*R*,2*R*,3*R*)-8].** A flame-dried round bottom flask equipped with a magnetic stirring bar, an argon inlet, and a rubber septum was charged with (1*R*,2*R*,3*R*)-**7** (dr = 82:11:7) (44.3 mg, 0.20 mmol), imidazole (273.7 mg, 4.0 mmol), and dry CH_2Cl_2 (2.5 mL). To the obtained mixture, a solution of TBSCl (606.2 mg, 4.0 mmol) in dry hexanes (2 mL) was added. The reaction mixture was stirred at room temperature overnight. After the complete consumption of (1*R*,2*R*,3*R*)-**7**, the reaction mixture was quenched with a saturated aqueous $NaHCO_3$ solution (10 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phase was washed with brine (10 mL), dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. Purification by column chromatography (EtOAc:hexanes, 1:4 v/v) gave (1*R*,2*R*,3*R*)-**8** (63.2 mg, 94% yield) with a 83:11:6 diastereomeric ratio; a colorless oil. R$_f$ 0.71 (EtOAc:hexanes, 1:4 v/v); $[\alpha]_D^{24}$ +36.9 (*c* 1.00, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (d, *J* 8.6 Hz, 2H, Ar*H*), 6.82 (d, *J* 8.6 Hz, 2H, Ar*H*), 5.90–5.78 (m, 1H, C*H*), 5.06–4.96 (m, 2H, C*HH*), 4.28 (d, *J* 8.6 Hz, 1H, C*H*), 3.80 (s, 3H, OC*H*$_3$), 2.86–2.75 (m, 1H, C*H*), 1.75–1.65 (m, 1H, C*H*), 1.05 (d, *J* 7.0 Hz, 3H, C*H*$_3$), 0.84 [s, 9H, SiC(C*H*$_3$)$_3$], 0.46 (d, *J* 7.0 Hz, 3H, C*H*$_3$), −0.00 (s, 3H, C*H*$_3$), −0.38 (s, 3H, C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8 (C), 140.9 (CH), 136.9 (C), 128.4 (2 × CH), 114.4 (CH_2), 113.4 (2 × CH), 77.6 (CH), 55.4 (OCH_3), 46.9 (CH), 36.7 (CH), 26.1 (3 × CH_3), 19.0 (CH_3), 18.3 (C), 11.0 (CH_3), −4.2 (CH_3), −4.8 (CH_3). IR (ATR): ν_{max} 1511s, 1461m, 1248s, 1172m cm^{-1}. MS: *m/z* (%) relative intensity 335 [(M)$^+$, 1], 251 (100), 121 (33), 55 (4). HRMS (ESI-TOF) calcd for $C_{20}H_{34}O_2SiNa$ [M + Na]$^+$: 357.2226, found: 357.2225.

(1*R*,2*S*,3*R*,4*R*)-1-[3,4-Bis(benzyloxy)phenyl]-4-[(tert-butyldimethylsilyl)oxy]-4-(4-methoxyphenyl)-2,3-dimethylbutan-1-ol [(1*R*,2*S*,3*R*,4*R*)-9a] and (1*S*,2*S*,3*R*,4*R*)-1-[3,4-Bis(benzyloxy)phenyl]-4-[(tert-butyldimethylsilyl)oxy]-4-(4-methoxyphenyl)-2,3-dimethylbutan-1-ol [(1*S*,2*S*,3*R*,4*R*)-9b]. To a suspension of (1*R*,2*R*,3*R*)-**8** (dr = 83:11:6) (146.7 mg, 0.44 mmol) and *N*-methylmorpholine-*N*-oxide (155.1 mg, 1.32 mmol) in CH_2Cl_2 (18 mL) were added OsO_4 (2.5% w/v in *t*-butanol, 0.22 mL, 0.022 mmol) and water (0.22 mL). After stirring at room temperature for 14 h, $NaIO_4$ (188.2 mg, 0.88 mmol) was added. The stirring was continued for 1.5 h, then the mixture was quenched with a saturated aqueous $Na_2S_2O_3$ solution (10 mL) and extracted with CH_2Cl_2 (3 × 15 mL). The combined organic phase was washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure to provide the aldehyde crude product which was used in the next step without further purification. A flame-dried round bottom flask equipped with a magnetic stirring bar, an argon inlet, and a rubber septum was charged with 4-bromo-1,2-benzyloxybenzene (339.7 mg, 0.92 mmol) and dry THF (3.5 mL). The solution was cooled at −78 °C and a solution of *n*-BuLi (1.6 M in hexanes, 0.58 mL, 0.92 mmol) was added dropwise. After stirring for 10 min, a solution of the above obtained aldehyde in dry THF (3.5 mL) was added dropwise. After stirring at −78 °C for 4 h, the reaction mixture was quenched with a saturated aqueous $NaHCO_3$ solution (10 mL) and extracted with EtOAc (3 × 15 mL). The combined organic phase was washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. Purification by column chromatography (EtOAc:hexanes, 1:9 v/v) provided (1*R*,2*S*,3*R*,4*R*)-**9a** (121.0 mg, 44% yield), (1*S*,2*S*,3*R*,4*R*)-**9b** (42.2 mg, 15% yield), and a mixture of other isomers (24.8 mg, 9% yield).

(1*R*,2*S*,3*R*,4*R*)-**9a**; a colorless oil; R$_f$ 0.25 (EtOAc:hexanes, 1:9 v/v); $[\alpha]_D^{28}$ +14.0 (*c* 1.72, CH_2Cl_2). ^{1}H NMR (400 MHz, acetone-*d*$_6$): δ 7.53–7.46 (m, 4H, Ar*H*), 7.40–7.34 (m, 4H, Ar*H*), 7.33–7.29 (m, 2H, Ar*H*), 7.22 (d, *J* 8.7 Hz, 2H, Ar*H*), 7.11 (d, *J* 1.8 Hz, 1H, Ar*H*), 7.02 (d, *J* 8.2 Hz, 1H, Ar*H*), 6.91 (dd, *J* 1.8, 8.3 Hz, 1H, Ar*H*), 6.86 (d, *J* 8.7

Hz, 2H, Ar*H*), 5.14 (s, 4H, 2 × C*H*$_2$), 4.97 (dd, *J* 4.6, 4.6 Hz, 1H, C*H*), 4.75 (d, *J* 6.8 Hz, 1H, C*H*), 3.99 (d, *J* 4.4 Hz, 1H, O*H*), 3.77 (s, 3H, OC*H*$_3$), 1.96–1.86 (m, 1H, C*H*), 1.71–1.62 (m, 1H, C*H*), 0.97 (d, *J* 6.9 Hz, 3H, C*H*$_3$), 0.90 [s, 9H, SiC(C*H*$_3$)$_3$], 0.79 (d, *J* 7.0 Hz, 3H, C*H*$_3$), 0.09 (s, 3H, C*H*$_3$), −0.24 (s, 3H, C*H*$_3$). ^{13}C NMR (100 MHz, acetone-*d*$_6$): δ 159.9 (C), 149.6 (C), 148.6 (C), 140.8 (C), 138.9 (2 × C), 136.7 (C), 129.3 (2 × CH), 129.2 (4 × CH), 128.5 (2 × CH), 128.4 (4 × CH), 120.3 (CH), 115.5 (CH), 114.6 (CH), 114.0 (2 × CH), 77.9 (CH), 74.4 (CH), 71.9 (CH$_2$), 71.8 (CH$_2$), 55.5 (OCH$_3$), 44.8 (CH), 43.9 (CH), 26.5 (3 × CH$_3$), 18.9 (C), 14.9 (CH$_3$), 11.5 (CH$_3$), −4.1 (CH$_3$), −4.4 (CH$_3$). IR (ATR): ν$_{max}$ 3380br, 1610m, 1509s, 1455m, 1248s, 1132m cm^{-1}. MS: *m/z* (%) relative intensity 347 (18), 319 (2), 251 (100), 176 (26), 91 (61). HRMS (ESI-TOF) calcd for $C_{39}H_{50}O_5SiNa$ [M + Na]$^+$: 649.3325, found: 649.3324.

(1*S*,2*S*,3*R*,4*R*)-**9b**; a colorless oil; R$_f$ 0.34 (EtOAc:hexanes, 1:9 v/v); $[\alpha]_D^{30}$ +30.2 (*c* 0.81, CH$_2$Cl$_2$). ^{1}H NMR (400 MHz, acetone-*d*$_6$): δ 7.53–7.47 (m, 4H, Ar*H*), 7.40–7.34 (m, 4H, Ar*H*), 7.34–7.27 (m, 4H, Ar*H*), 7.11 (d, *J* 1.4 Hz, 1H, Ar*H*), 6.99 (d, *J* 8.2 Hz, 1H, Ar*H*), 6.92 (d, *J* 8.6 Hz, 2H, Ar*H*), 6.87 (dd, *J* 1.4, 8.2 Hz, 1H, Ar*H*), 5.15 (s, 4H, 2 × C*H*$_2$), 4.99 (d, *J* 7.8 Hz, 1H, C*H*), 4.47 (s, 1H, O*H*), 4.43 (d, *J* 9.8 Hz, 1H, C*H*), 3.79 (s, 3H, OC*H*$_3$), 2.25–2.15 (m, 1H, C*H*), 2.09–1.96 (m, 1H, C*H*), 0.92 [s, 9H, SiC(C*H*$_3$)$_3$], 0.81 (d, *J* 7.2 Hz, 3H, C*H*$_3$), 0.57 (d, *J* 7.1 Hz, 3H, C*H*$_3$), 0.18 (s, 3H, C*H*$_3$), −0.24 (s, 3H, C*H*$_3$). ^{13}C NMR (100 MHz, acetone-*d*$_6$): δ 160.2 (C), 150.1 (C), 149.5 (C), 140.9 (C), 139.3 (C), 139.1 (C), 138.3 (C), 129.6 (4 × CH), 129.5 (2 × CH), 129.0 (CH), 128.9 (CH), 128.8 (2 × CH), 128.7 (2 × CH), 121.6 (CH) 115.8 (CH), 115.4 (CH), 114.5 (2 × CH), 79.9 (CH), 77.4 (CH), 72.2 (2 × CH$_2$), 55.9 (OCH$_3$), 47.1 (CH), 41.5 (CH), 26.9 (3 × CH$_3$), 19.3 (C), 17.6 (CH$_3$), 13.5 (CH$_3$), −3.6 (CH$_3$), −3.9 (CH$_3$). IR (ATR): ν$_{max}$ 3379br, 1610m, 1510s, 1455m, 1248s, 1133m cm^{-1}. MS: *m/z* (%) relative intensity 251 (100), 176 (45), 91 (62). HRMS (ESI-TOF) calcd for $C_{39}H_{50}O_5SiNa$ [M + Na]$^+$: 649.3325, found: 649.3328.

(1*R*,2*S*,3*R*,4*R*)-1-[3,4-Bis(benzyloxy)phenyl]-4-(4-methoxyphenyl)-2,3-dimethylbutane-1,4-diol [(1*R*,2*S*,3*R*,4*R*)-1a]. A solution of TBAF (26.7 mg, 0.085 mmol) in THF (1 mL) was added to a solution of (1*R*,2*S*,3*R*,4*R*)-**9a** (53.0 mg, 0.085 mmol) in THF (1 mL) at room temperature. After stirring for 3 h, the reaction mixture was quenched with H$_2$O (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic phase was washed with brine (10 mL) and dried over anhydrous Na$_2$SO$_4$. After removal of solvents, the crude product was purified by column chromatography (EtOAc:hexanes, 2:3 v/v) to provide (1*R*,2*S*,3*R*,4*R*)-**1a** (37.3 mg, 73% yield) as a single diastereomer; a colorless sticky oil. R$_f$ 0.33 (EtOAc:hexanes, 2:3 v/v); $[\alpha]_D^{28}$ −4.9 (*c* 1.71, CH$_2$Cl$_2$). ^{1}H NMR (400 MHz, acetone-*d*$_6$): δ 7.54–7.48 (m, 4H, Ar*H*), 7.40–7.33 (m, 4H, Ar*H*), 7.33–7.29 (m, 2H, Ar*H*), 7.26 (d, *J* 8.5 Hz, 2H, Ar*H*), 7.20 (s, 1H, Ar*H*), 7.03–6.96 (m, 2H, Ar*H*), 6.88 (d, *J* 8.6 Hz, 2H, Ar*H*), 5.16 (s, 2H, C*H*$_2$), 5.15–5.11 (m, 3H, C*H*$_2$ and O*H*), 5.05 (broad s, 1H, O*H*), 4.96 (s, 1H, C*H*), 4.42 (d, *J* 9.6 Hz, 1H, C*H*), 3.77 (s, 3H, OC*H*$_3$), 2.04–1.98 (m, 1H, C*H*), 1.97–1.87 (m, 1H, C*H*), 0.91 (d, *J* 7.1 Hz, 3H, C*H*$_3$), 0.66 (d, *J* 7.0 Hz, 3H, C*H*$_3$). ^{13}C NMR (100 MHz, acetone-*d*$_6$): δ 159.9 (C), 149.5 (C), 148.5 (C), 140.7 (C), 139.0 (C), 138.9 (C), 138.2 (C), 129.2 (4 × CH), 129.1 (2 × CH), 128.5 (4 × CH), 128.4 (2 × CH), 120.0 (CH), 115.4 (CH), 114.4 (CH), 114.3 (2 × CH), 76.7 (CH), 76.1 (CH), 71.8 (CH$_2$), 71.7 (CH$_2$), 55.5 (OCH$_3$), 47.2 (CH), 45.7 (CH), 18.1 (CH$_3$), 7.9 (CH$_3$). IR (ATR): ν$_{max}$ 3613br, 3257br, 1613m, 1510s, 1457m, 1243s, 1123m cm^{-1}. MS: *m/z* (%) relative intensity 360 (4), 268 (3), 165 (2), 161 (74), 137 (1), 91 (100). HRMS (ESI-TOF) calcd for $C_{33}H_{36}O_5Na$ [M + Na]$^+$: 535.2460, found: 535.2462.

(1*S*,2*S*,3*R*,4*R*)-1-[3,4-Bis(benzyloxy)phenyl]-4-(4-methoxyphenyl)-2,3-dimethylbutane-1,4-diol [(1*S*,2*S*,3*R*,4*R*)-1b]. According to the procedure for the synthesis of (1*R*,2*S*,3*R*,4*R*)-**1a**, treatment of (1*S*,2*S*,3*R*,4*R*)-**9b** (21.1 mg, 0.034 mmol) with a solution of TBAF (10.6 mg, 0.034 mmol) in THF (1 mL) gave (1*S*,2*S*,3*R*,4*R*)-**1b** (12.4 mg, 71% yield) as a single diastereomer after purification by column chromatography (EtOAc:hexanes, 2:3 v/v); a white solid. Mp. 118–120 °C (EtOAc:hexanes, 2:3 v/v). R$_f$ 0.22 (EtOAc:hexanes, 2:3 v/v); $[\alpha]_D^{26}$ +11.6 (*c* 1.24, CH$_2$Cl$_2$). ^{1}H NMR (400 MHz, acetone-*d*$_6$): δ 7.55–7.48 (m, 4H, Ar*H*), 7.40–7.33 (m, 4H, Ar*H*), 7.33–7.29 (m, 2H, Ar*H*), 7.27 (d, *J* 8.6 Hz, 2H, Ar*H*), 7.11 (d, *J* 1.8 Hz, 1H, Ar*H*), 7.01 (d, *J* 8.2 Hz, 1H, Ar*H*), 6.91–6.82 (m, 3H, Ar*H*), 5.41 (d, *J* 4.1 Hz, 1H, O*H*), 5.37 (d, *J* 3.9 Hz, 1H, O*H*), 5.16 (s, 2H, C*H*$_2$), 5.14 (s, 2H, C*H*$_2$), 4.56–4.49 (m, 2H, 2 × C*H*), 3.76 (s, 3H, OC*H*$_3$), 2.08–1.96 (m, 2H, 2 × C*H*), 0.78 (d, *J* 6.8 Hz, 3H, C*H*$_3$), 0.76 (d, *J* 6.7 Hz, 3H, C*H*$_3$). ^{13}C NMR (100 MHz, acetone-*d*$_6$): δ 159.9 (C), 150.0 (C), 149.2 (C), 140.4 (C), 139.2 (C), 139.1 (C), 138.9 (C), 129.6 (4 × CH), 129.1 (2 × CH), 128.9 (2 × CH), 128.8 (2 × CH), 128.7 (2 × CH), 120.9 (CH), 115.7 (CH), 115.0 (CH), 114.5 (2 × CH), 76.9 (CH), 76.7 (CH), 72.1 (CH$_2$), 72.0 (CH$_2$), 55.8 (OCH$_3$), 43.6 (CH), 43.5 (CH), 16.1 (CH$_3$), 15.9 (CH$_3$). IR (ATR): ν$_{max}$ 3406br, 1610m, 1514s, 1454m, 1249s, 1134m cm^{-1}. MS: *m*/*z* (%) relative intensity 360 (7), 268 (2), 165 (2), 161 (60), 137 (10), 91 (100). HRMS (ESI-TOF) calcd for $C_{33}H_{36}O_5Na$ [M + Na]$^+$: 535.2460, found: 535.2461.

(2*S*,3*S*,4*R*,5*R*)-2-[3,4-Bis(benzyloxy)phenyl]-5-(4-methoxyphenyl)-3,4-dimethyltetrahydrofuran [(2*S*,3*S*,4*R*,5*R*)-3a]. A solution of (1*R*,2*S*,3*R*,4*R*)-**1a** (37.3 mg, 0.073 mmol) in CH$_2$Cl$_2$ (2 mL) was treated with *p*-TsOH·H$_2$O (4 mg, 0.02 mmol) at room temperature. After stirring for 40 min, the reaction mixture was quenched with a saturated aqueous NaHCO$_3$ solution (3 mL) and extracted with CH$_2$Cl$_2$ (3 × 10 mL). The combined organic phase was washed with brine (10 mL) and dried over anhydrous Na$_2$SO$_4$. After removal of the solvent *in vacuo*, (2*S*,3*S*,4*R*,5*R*)-**3a** was obtained (32.3 mg, 89% yield) as a single diastereomer; a colorless sticky oil. R$_f$ 0.54 (EtOAc:hexanes, 2:3 v/v); $[\alpha]_{D}^{28}$ +4.9 (*c* 0.99, CH$_2$Cl$_2$). ^{1}H NMR (400 MHz, acetone-*d*$_6$): δ 7.51 (d, *J* 7.8 Hz, 4H, Ar*H*), 7.41–7.34 (m, 6H, Ar*H*), 7.34–7.28 (m, 2H, Ar*H*), 7.18 (d, *J* 1.8 Hz, 1H, Ar*H*), 7.05 (d, *J* 8.2 Hz, 1H, Ar*H*), 6.99 (dd, *J* 1.8, 8.2 Hz, 1H, Ar*H*), 6.96–6.90 (m, 2H, Ar*H*), 5.18 (s, 2H, C*H*$_2$), 5.16 (s, 2H, C*H*$_2$), 4.43 (d, *J* 7.2 Hz, 1H, C*H*), 4.41 (d, *J* 6.8 Hz, 1H, C*H*), 3.79 (s, 3H, OC*H*$_3$), 2.26–2.16 (m, 2H, 2 × C*H*), 0.99 (d, *J* 6.6 Hz, 3H, C*H*$_3$), 0.98 (d, *J* 6.6 Hz, 3H, C*H*$_3$). ^{13}C NMR (100 MHz, acetone-*d*$_6$): δ 160.5 (C), 150.3 (C), 149.7 (C), 139.2 (C), 139.1 (C), 137.5 (C) 135.8 (C), 129.6 (4 × CH), 128.9 (2 × CH), 128.8 (4 × CH), 128.7 (2 × CH), 120.5 (CH), 116.0 (CH), 114.9 (2 × CH), 114.5 (CH), 88.3 (CH), 88.1 (CH), 72.1 (CH$_2$), 72.0 (CH$_2$), 55.9 (OCH$_3$), 46.1 (CH), 45.8 (CH), 13.6 (CH$_3$), 13.3 (CH$_3$). IR (ATR): ν$_{max}$ 1610m, 1510s, 1454m, 1245s, 1131m cm^{-1}. MS: *m*/*z* (%) relative intensity 494 (M$^+$, 6), 239 (3), 135 (3), 91 (100). HRMS (ESI-TOF) calcd for $C_{33}H_{34}O_4Na$ [M + Na]$^+$: 517.2355, found: 517.2356.

(2*S*,3*S*,4*R*,5*R*)-2-(3,4-Dihydroxyphenyl)-5-(4-methoxyphenyl)-3,4-dimethyltetrahydrofuran [(2*S*,3*S*,4*R*,5*R*)-10]. A flame-dried round bottom flask equipped with a magnetic stirring bar, an argon inlet, and a rubber septum was charged with (2*S*,3*S*,4*R*,5*R*)-**3a** (11.5 mg, 0.023 mmol), Pd/C (10% w/w, 5 mg, 0.05 mmol), and dry EtOAc (2 mL). An argon inlet was replaced with H$_2$ balloon, and the reaction mixture was stirred at room temperature for 40 min. After the complete consumption of (2*S*,3*S*,4*R*,5*R*)-**3a**, the reaction mixture was filtered through a Celite pad eluted with EtOAc (10 mL). After evaporation, the crude product was purified by column chromatography (EtOAc:hexanes, 2:3 v/v) to provide (2*S*,3*S*,4*R*,5*R*)-**10** as a sticky brownish oil (5.1 mg, 71% yield) as a single diastereomer. R$_f$ 0.34 (EtOAc:hexanes, 2:3 v/v); $[\alpha]_{D}^{26}$ +5.7 (*c* 0.88, CH$_2$Cl$_2$). ^{1}H NMR (400 MHz, acetone-*d*$_6$): see Table 1. ^{13}C NMR (100 MHz, acetone-*d*$_6$): see Table 1. IR (ATR): ν$_{max}$ 3294br, 1611m, 1512s, 1243s, 1172s cm^{-1}. MS: *m*/*z* (%) relative intensity 178 (78), 176 (44), 164 (29), 162 (23). HRMS (ESI-TOF) calcd for $C_{19}H_{22}O_4Na$ [M + Na]$^+$: 337.1416, found: 337.1418.

Acknowledgements

The authors acknowledge financial support from the Thailand Research Fund (RSA6180025 and IRN58W0005), the Center of Excellence for Innovation in Chemistry (PERCH-CIC), Ministry of Higher Education, Science, Research and Innovation, and the Office of the Higher Education Commission and Mahidol University under the National Research Universities Initiative. The Science Achievement Scholarship of Thailand (SAST) is also gratefully acknowledged for financial support through student scholarship to R. C.

Supplementary Material

Copies of ^{1}H and ^{13}C NMR spectra of all compounds as well as NOESY experiments of (2*S*,3*S*,4*R*,5*R*)-**3a** and (2*S*,3*S*,4*R*,5*R*)-**10** are available in the Supplementary Material associated with this manuscript in the online version of the text.

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