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Neighboring Lithium-Assisted [1,2]-Wittig Rearrangement: Practical Access to Diarylmethanol-Based 1,4-Diols and Optically Active BINOL Derivatives with Axial and sp^3-Central Chirality

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Abstract: A facile and practical methodology for the synthesis of synthetically useful diarylmethanol-based 1,4-diols and enantiomerically pure BINOL-derived diols with axial and sp^3-central chirality has been developed through neighboring lithium-promoted [1,2]-Wittig rearrangement. The chirality transfer process shows a broad substrate scope in terms of the aromatic ether substituent, which allows access to a broad of range of chiral 1,1′-binaphthalene-2-α-arylmethanol-2′-ols with excellent enantioselectivities (>99% enantiomeric excess) and yields (84–96%). This should be considered as an available and attractive chiral source to design and prepare privileged ligands or catalysts.

Keywords: asymmetric synthesis · chirality · chirality transfer · diols · Wittig rearrangement

Introduction

The [1,2]-Wittig rearrangement is a classic rearrangement through a 1,2-alkyl shift onto an α-oxycarbanion terminus, which proceeds by a radical dissociation–recombination mechanism.[1] The first example of Wittig rearrangement was reported in 1942[2] and since then the transformation has attracted much interest from both a mechanistic and synthetic point of view.[3] Unfortunately, although the [1,2]-Wittig rearrangement is recognized as a powerful method for carbon–carbon bond-forming reactions and there are many reports on mechanistic or stereochemical studies, the utility of the [1,2]-Wittig rearrangement in organic synthesis has been limited by low yields, the restricted range of suitable substrates, and the lack of good stereocontrol.[4] Few successes have been reported in the area of asymmetric synthesis; however, the enantioselective [1,2]-Wittig rearrangement was shown to be of particular value for the construction of chiral alcohols and their analogues from ethers or acetal compounds, with retention of configuration at the migrating carbon atom.[5] Thus, it would be highly desirable to develop an enantioselective [1,2]-Wittig rearrangement that could be used in the preparation of synthetically useful chiral products. Herein, we report the [1,2]-Wittig rearrangement of two different types of phenol benzyl ethers, based on a neighboring lithium-promoted process, which results in synthetically useful diarylmethanol-based 1,4-diols and enantiomerically pure BINOL-derived diols with axial and sp^3-central chirality.

The facile preparation of unsymmetrical diols is an important and challenging goal in synthetic chemistry, because they are versatile building blocks for complex natural molecules.[6] In particular, 1,4-diols (including diarylmethanol-based 1,4-diols) are widely used for the preparation of important heterocycles, such as γ-lactones, pyrroles, and tetrahydrofurans, and therapeutically relevant compounds, for example, the antidepressant drug escitalopram.[7] Despite the proposal of various modified methods for the synthesis of 1,4-diols in the last decade, some of these still suffer from drawbacks in the key step, such as low yields, employment of expensive chemicals, tedious procedures, or multiple steps. Hence, development of new methodology to simultaneously address these issues was desirable.

Results and Discussion

Our interest in the use of 2-benzyloxyphenylmethanol (**3a**) as a scaffold originates from salicylaldehyde (**1**) alkylation and reduction.[8] We are particularly attracted to the ability of the terminal alcohol moiety to induce an aggregate lithium ion around the α-carbon center of the benzyl moiety, which is beneficent to the lithiation and subsequent [1,2]-

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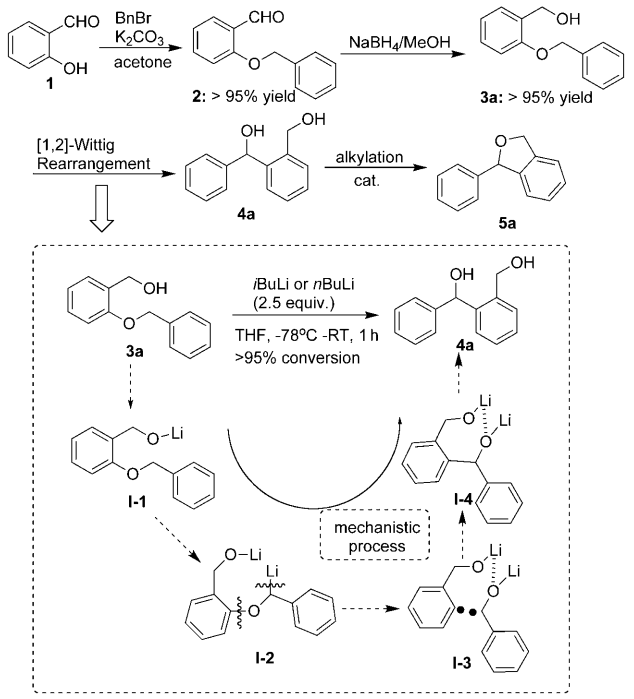


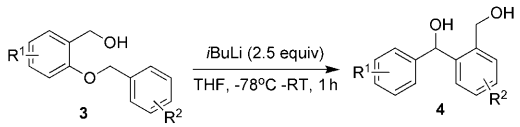
Scheme 1. [1,2]-Wittig rearrangement of 2-benzyloxy-phenylmethanol (**3a**).

Wittig rearrangement (Scheme 1). We envisioned that an intramolecular neighboring lithium atom would be a useful linker for the subsequent intramolecular-like radical dissociation–recombination. The results of this preliminary study were instructive. Initial experiments demonstrated that the clean reaction of **3a** with *i*BuLi or *n*BuLi in THF afforded, as expected, the diphenylmethanol-based 1,4-diol **4a** with a high yield (Scheme 1, 91%).

With these observations in hand, attention was turned to the key question of reaction scope. The requisite starting materials **3** were readily prepared by benzylation, followed by reduction. Eight further substrates were examined in the [1,2]-Wittig rearrangement under the optimized conditions and the results are summarized in Table 1. The intramolecular lithium-induced [1,2]-Wittig rearrangement to diarylmethanol-based diols tolerates a range of substituents on the aromatic ring and, in most cases, the diols were obtained in good yields. Interestingly, the presence of a chlorine substituent was not problematic (Table 1, entry 2), which is significant as it allows for the introduction of a potential handle for further functionalization of the diols. A 4-methoxy substituent was well tolerated (Table 1, entry 6), whereas the presence of the methoxy group in the 5-position resulted in low yield (Table 1, entry 7). We suspect that this is due to the restrictive effect of the *para*-methoxy substituent on the cleavage of the C–O bond and subsequent formation of the radical intermediate.

Inspired by this success, the previous examples of enantioselective [1,2]-Wittig rearrangement,[9] and on the basis of the unique structure of binaphthyl compounds, our focus

Table 1. Scope of the [1,2]-Wittig rearrangement of **3** to diarylmethanol-based diols **4**.[a]



Entry	R^1	R^2	Product	Yield [%][b]
1	H	H	**4a**	91
2	5-Cl	H	**4b**	64
3	H	4-Me	**4c**	74
4	H	4-*t*Bu	**4d**	85
5	H	2-Me	**4e**	81
6	4-OMe	H	**4f**	72
7	5-OMe	H	**4g**	31
8	4-OMe	4-Me	**4h**	76
9	4-OMe	4-*t*Bu	**4i**	58

[a] Reagents and conditions: A solution of *i*BuLi (1.23 M in hexane, 2.5 equiv) was added to **3** (5 mmol) in anhydrous THF (30 mL) at −78 °C under N_2; stirred at RT for 1 h. [b] Isolated yield.

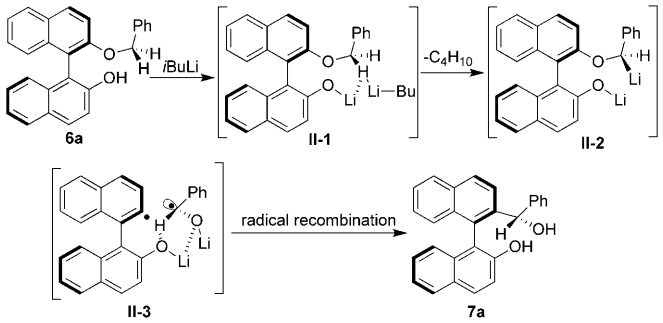
was shifted to the development of a highly efficient enantioselective [1,2]-Wittig rearrangement through chirality transfer from C_2-axial 1,1′-binaphthalene-2,2′-diol (BINOL) to BINOL-derived alcohols that contained a stereogenic tetrahedral carbon center. Specifically, we were interested in the application of a modified [1,2]-Wittig rearrangement in the synthesis of novel BINOL-derived enantiomerically pure ligands and organocatalysts.

The preparation of structurally diverse chiral compounds from simple and readily available starting materials is an important goal and challenge in organic chemistry.[10] Hence, over the past three decades, the synthesis of enantiopure compounds has emerged as one of the most active fields in organic synthesis. Numerous well-documented cases highlight the necessity for the development of asymmetric synthesis and successful stereoselective reactions.[11] In the field of asymmetric synthesis, BINOL and its derivatives, for example, 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP), have been arguably the most widely used as a source of chirality for both stoichiometric and catalytic asymmetric reactions.[12]

Among many successful ligands and organocatalysts, axially chiral biaryls, with both axial and sp^3-central chirality, comprise a very interesting and attractive area of research. The presence of an additional chiral center on the biaryl framework was found to exert significant influences on the biological activity of axially chiral biaryl natural products[13] and the enantioselectivity and activity of the catalysts in asymmetric reactions.[14] However, to the best of our knowledge to date, there are few successful enantioselective syntheses of 2,2′-disubstituted-1,1′-binaphthyls that contain two chiral elements through axial-to-central chirality transfer.

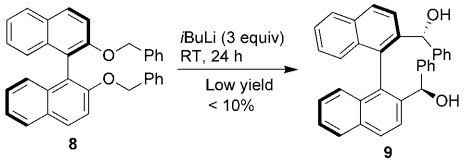
There are only a few reported successes of the asymmetric synthesis of enantiomerically pure BINOL derivatives with axial and sp^3-central chirality. An axial-to-central chirality transfer approach is of particular value for the improvement of the enantioselectivity. Such an approach is highly desira-

ble and is not trivial. With knowledge of the mechanism of the [1,2]-Wittig rearrangement, we assumed that the existence of a lithium salt in the same molecule could promote the one-pot enantioselective [1,2]-Wittig rearrangement through a well-known radical dissociation-recombination mechanism. As shown in Scheme 2, the intramolecularly as-



Scheme 2. Hypothesis of neighboring lithium-assisted [1,2]-Wittig rearrangement of monobenzyl BINOL derivative **6a**.

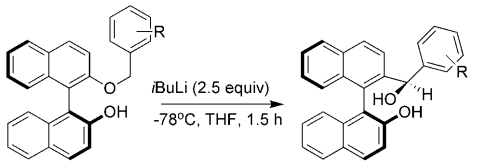
sembled dimeric lithium intermediate (**II-1**→**II-2**→**II-3**) induces the radical to generate an enantiomerically pure BINOL derivative with axial and sp^3-central chirality via a five-membered transition state, with the aid of hydrogen bonding and the aggregation of a lithium moiety. Comparably, when a solution of 2,2′-di(2-benzyloxy)-1,1′-binaphthyl (**8**) in tetrahydrofuran was treated under the optimized conditions described above, the desired diol, 1,1-(1,1′-binaphth-2,2′-diyl)-bis(2-phenylmethanol) (**9**), was isolated in a very low yield (<10%, Scheme 3), but as a single isomer in excellent (>99%) enantiomeric excess (*ee*). In agreement with the mechanism proposed in Scheme 2, the rearrangement must be slow without the activation by the intramolecular lithium salt, hence, only a trace of the desired product and at least three byproducts were detected.



Scheme 3. [1,2]-Wittig rearrangement of 2,2′-di(2-benzyloxy)-1,1′-binaphthyl (**8**).

The scope of the [1,2]-Wittig rearrangement under the optimized conditions was studied with a set of substituted aryl ether derivatives of (*S*)-BINOL (Table 2). As indicated by the results presented in Table 2, the [1,2]-Wittig rearrangement shows a remarkably wide scope and functional group tolerance, which allows the reaction to be carried out in the presence of any functionalities that are compatible with the organolithium reagent. To our delight, variation of the substituent R in the monosubstituted aryl ether of BINOL **6** had only a small impact on the axial-to-central chirality transfer and, in all cases, almost complete asymmetric induction ($ee \geq 99\%$) was obtained. It is worth noting that all of the 1,1′-binaphthalene-2-α-arylmethan-2′-ol (Ar-BINMOL) products **7** could be prepared on a multigram scale without loss of enantioselectivity, which would be beneficial to the preparation and application of novel ligands and catalysts based on this scaffold. Consistent with this conclusion, the reaction of racemic starting materials under the optimized conditions resulted in the almost quantitative formation of only two isomers, (S_A,R_C)-**7** and (R_A,S_C)-**7**. Thus, it is interesting to study the subsequent formation of (S_A,S_C)-**7** or (R_A,R_C)-**7** through simple transformations. However, attempts to prepare (S_A,S_C)-**11** from (S_A,R_C)-**7b** led to a mixture of two stereoisomers in enantiomeric ratios between 67:33 and 92:8 (S_A,R_C)-**7b**/(S_A,S_C)-**11**, dependent on the reducing agent. These reductions of ketone derivative **10** revealed it is difficult to convert (S_A,R_C)-**7b** to (S_A,S_C)-**11** by an oxidation/reduction procedure (Scheme 4).

Table 2. Scope of the enantioselective [1,2]-Wittig rearrangement of **6** to Ar-BINMOLs **7**.[a]

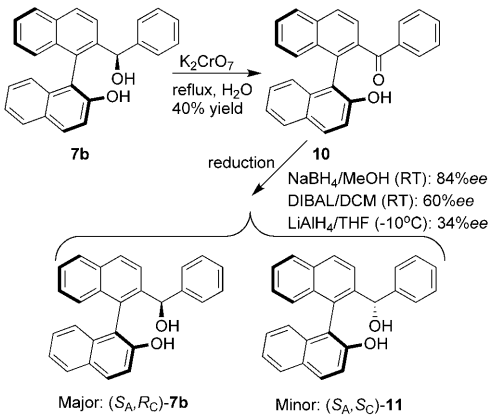


Entry	R	Product	Yield [%][b]	*ee* [%][c]
1	H	**7b**	95	99.1
2	H	**7a**	96	>99.9[d]
3	3,5-(tBu)$_2$	**7c**	88	98.9
4	p-CH$_3$	**7d**	94	99.6
5	p-F	**7e**	84	99.7
6	o-CH$_3$	**7f**	93	99.4
7	o-OCH$_3$	**7g**	94	>99.9
8	m-OCH$_3$	**7h**	93	>99.9
9	p-OCH$_3$	**7i**	87	99.5
10	2-Np	**7k**	93	99.9
11	p-SiMe$_3$	**7l**	88	>99.9
12	p-tBu	**7m**	89	99.6

[a] Reaction conditions: (*S*)-BINOL derivative **6** (2 mmol), *i*BuLi or *n*-BuLi (5 mmol, 1.23 M in pentane, 2.5 equiv), THF (20 mL); −78 °C; 1.5 h. [b] Isolated yield. [c] Enantiomeric excess was determined by chiral HPLC analysis. [d] Reaction with the monosubstituted aryl ether of (*R*)-BINOL; see Scheme 2 for stereochemistry of the product **7a**.

Conclusion

The facile and practical methodology described converts simple and readily accessible benzyl ethers and axially chiral monoalkylated BINOLs into synthetically useful diarylmethanol-based 1,4-diols and enantiomerically pure BINOL-derived diols with axial and sp^3-central chirality, respectively, through axial-to-central chiral transfer, respectively. The chirality transfer process shows very broad substrate scope in terms of the aromatic ether, with excellent



Scheme 4. The enantioselective transformation of **7b** by oxidation and reduction.

enantioselectivities and yields, which allows access to a broad range of chiral Ar-BINMOLs. This should be considered as an available and attractive chiral source for the design and preparation of privileged ligands or catalysts. Further studies directed towards the preparation and application of new ligands and catalysts based on this scaffold are currently underway.

Experimental Section

Flash column chromatography was performed on silica gel (200–300 mesh). ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, by using a Bruker Avance 400 MHz spectrometer and were referenced to the internal solvent signals. TLC was performed on silica gel F254 TLC plates and visualization was performed with ultraviolet light. HPLC was carried out by using a Waters 2695 Millennium chromatography system equipped with a photodiode array detector. EI and CI mass spectra were performed with a Trace DSQ GC/MS spectrometer. Substrate **1**, isobutyllithium, and *n*-butyllithium were commercially available and used directly. The structures of known [1,2]-Wittig rearrangement products were confirmed by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy. ESI-MS analysis was performed on an LCQ Advantage mass spectrometer (ThermoFisher Company, USA), equipped with an ESI ion source in the positive ionization mode, with data acquisition using the Xcalibur software (Version 1.4). UV/Vis absorption and circular dichroism spectra were recorded on MOS-450/AF-CD and Evolution-300 spectrometers, respectively.

General procedure for the [1,2]-Wittig rearrangement of 3: *i*BuLi (1.23 M in hexane, 2.5 equiv) was added to a solution of **3** (5 mmol) in anhydrous THF (30 mL) under N_2 at −78 °C. The mixture was allowed to warm slowly to RT, then the mixture was stirred at RT for 1 h. After the reaction was complete, the reaction was quenched with water and extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (petroleum ether/EtOAc 4:1) to afford the pure diol **4** (Table 1).

Diol 4a: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.26 (d, J = 12.0 Hz, 1H), 4.43 (d, J = 12.0 Hz, 1H), 5.91 (s, 1H), 7.19–7.36 ppm (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 63.4, 73.9, 126.5, 127.3, 128.2, 128.3, 128.3, 128.8, 130.1, 138.4, 142.3, 142.6 ppm; IR (KBr): $\tilde{\nu}$ = 3249, 2951, 1493, 1442, 999 cm^{-1}; MS (ESI$^-$): m/z: 449 $[2M+Na-2H]^-$.

Diol 4b: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.28 (d, J = 12.8 Hz, 1H), 4.43 (d, J = 12.8 Hz, 1H), 5.83 (s, 1H), 7.11–7.32 ppm (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 62.6, 73.1, 125.5, 127.7, 128.1, 128.5, 129.5, 129.9, 133.7 ppm; IR (KBr): $\tilde{\nu}$ = 3282, 2909, 1598, 1012, 700 cm^{-1}; MS (ESI$^-$): m/z: 517 $[2M+Na-2H]^-$.

Diol 4c: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.38 (s, 3H), 4.40 (d, J = 12.0 Hz, 1H), 4.54 (d, J = 12.0 Hz, 1H), 5.83 (s, 1H), 7.11–7.32 ppm (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2, 63.5, 73.9, 126.5, 127.1, 128.1, 128.3, 128.7, 129.0, 129.3, 130.1, 137.0, 137.9, 139.7, 142.4 ppm; IR (KBr): $\tilde{\nu}$ = 3250, 1482, 1103, 1052, 1022, 1013, 821 cm^{-1}; MS (ESI$^+$): m/z: 549 $[2M+Na]^+$.

Diol 4d: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.35 (s, 9H), 4.42 (d, J = 12.0 Hz, 1H), 4.56 (d, J = 12.0 Hz, 1H), 5.95 (s, 1H), 7.24–7.38 ppm (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.4, 63.6, 125.3, 126.2, 128.1, 128.3, 128.7, 130.1, 138.5, 139.6, 142.3, 150.3 ppm; IR (KBr): $\tilde{\nu}$ = 3270, 2965, 1457, 1103, 1017, 758 cm^{-1}; MS (ESI$^-$): m/z: 561 $[2M+Na-2H]^-$.

Diol 4e: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.04 (s, 3H), 4.52 (d, J = 10.4 Hz, 1H), 4.87 (d, J = 8.4 Hz, 1H), 6.16 (s, 1H), 6.90–7.58 ppm (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.2, 63.9, 70.3, 126.1, 126.2, 127.5, 127.9, 128.2, 128.5, 129.8, 130.4, 135.2, 138.9, 140.1 ppm; IR (KBr): $\tilde{\nu}$ = 3289, 3066, 2894, 1602, 1460, 1022, 898 cm^{-1}; MS (ESI$^-$): m/z: 477 $[2M+Na-2H]^-$.

Diol 4f: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.71 (s, 3H), 4.31 (d, J = 12.0 Hz, 1H), 4.45 (d, J = 12.0 Hz, 1H), 5.88 (s, 1H), 6.74–7.32 ppm (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.2, 62.9, 73.8, 112.4, 115.0, 126.5, 127.5, 128.3, 130.7, 131.7, 142.6, 144.0, 159.4 ppm; IR (KBr): $\tilde{\nu}$ = 3336, 2918, 2850, 1609, 1496, 1457, 1259, 1018 cm^{-1}; MS (ESI$^+$): m/z: 511 $[2M+Na]^+$.

Diol 4g: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.78 (s, 3H), 4.42 (d, J = 12.4 Hz, 1H), 4.59 (d, J = 12.4 Hz, 1H), 5.96 (s, 1H), 6.75–7.34 ppm (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.3, 63.7, 73.7, 112.8, 115.8, 126.4, 127.3, 128.3, 130.3, 134.4, 140.2, 142.9, 159.2 ppm; IR (KBr): $\tilde{\nu}$ = 3334, 2918, 2849, 1608, 1496, 1016 cm^{-1}; MS (ESI$^+$): m/z: 511 $[2M+Na]^+$.

Diol 4h: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.34 (s, 3H), 3.74 (s, 3H), 4.36 (d, J = 12.0 Hz, 1H), 4.51 (d, J = 12.0 Hz, 1H), 5.90 (s, 1H), 6.75–7.22 ppm (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1, 55.3, 63.1, 74.0, 112.3, 115.0, 126.4, 129.1, 130.7, 131.7, 137.1, 139.5, 144.1, 159.4 ppm; IR (KBr): $\tilde{\nu}$ = 3334, 2923, 1611, 1506, 1017 cm^{-1}; MS (ESI$^+$): m/z: 539 $[2M+Na]^+$.

Diol 4i: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32 (s, 9H), 3.76 (s, 3H), 4.39 (d, J = 12.0 Hz, 1H), 4.53 (d, J = 12.0 Hz, 1H), 5.94 (s, 1H), 6.79–7.36 ppm (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.4, 34.5, 55.3, 63.2, 74.1, 112.3, 115.1, 125.3, 126.2, 130.7, 131.7, 139.4, 144.0, 150.4, 159.5 ppm; IR (KBr): $\tilde{\nu}$ = 3281, 2956, 1611, 1280, 1043, 1022 cm^{-1}; MS (ESI$^+$): m/z: 539 $[2M+Na]^+$.

Typical procedure for enantioselective [1,2]-Wittig rearrangement of 6: *i*BuLi (1.23 M in pentane, 5 mmol) was added by syringe to a solution of (*S*)-**6** (2 mmol) in THF (20 mL) maintained at −78 °C. The reaction mixture was stirred at −78 °C for 1.5 h and then treated with saturated aqueous NH_4Cl solution. The resultant mixture was extracted with diethyl ether (×3) and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by chromatography on silica gel (petroleum ether/EtOAc 10:1) to give the desired product **7** (Table 2).

Enantiomeric diols 7a and b: $[\alpha]_D^{25}$ (**7a**, c = 1.20 in CH_2Cl_2) = −265.82; $[\alpha]_D^{25}$ (**7b**, c = 1.20 in CH_2Cl_2) = +254.44; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.26 (s, 1H), 5.60 (s, 1H), 6.38 (s, 1H), 6.80 (d, J = 8.4 Hz, 2H), 7.01–7.32 (m, 7H), 7.39–7.47 (m, 2H), 7.72–7.82 ppm (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 73.4, 117.2, 118.0, 123.6, 125.0, 126.1, 126.5, 126.6, 126.7, 127.1, 128.1, 128.1, 129.6, 130.2, 133.0, 133.4, 134.1, 141.4, 142.5, 151.3 ppm; IR (KBr): $\tilde{\nu}$ = 3379, 3056, 2954, 1944, 1619, 1595, 1507, 1341, 1268, 1237, 1143, 1012 cm^{-1}.

Diol 7c: $[\alpha]_D^{25}$ (c = 1.36 in CH_2Cl_2) = +195.24; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.14 (s, 18H), 2.74 (s, 1H), 5.67 (s, 1H), 5.76 (d, J = 4.4 Hz, 1H), 6.78 (d, J = 8.4 Hz, 1H), 6.85 (d, J = 1.2 Hz, 2H), 7.05 (t, J = 7.2 Hz, 1H), 7.13 (t, J = 8.8 Hz, 2H), 7.24 (m, 3H), 7.44 (t, J = 6.8 Hz, 1H), 7.66 (d, J = 8.8 Hz, 1H), 7.82 ppm (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): 31.4, 34.8, 73.8, 117.0, 117.9, 120.4, 121.2, 123.4, 125.1, 125.2, 126.4, 126.6, 126.7, 126.8, 128.07, 128.14, 129.1, 129.5, 129.7, 130.1, 133.0, 134.1, 141.8,

142.0, 150.5, 151.2 ppm; IR (KBr): $\tilde{\nu}$ = 3500, 3058, 2962, 2902, 1621, 1596, 1508, 1433, 1362, 1344 cm^{-1}.

Diol 7d: $[\alpha]_D^{25}$ (c = 1.20 in CH_2Cl_2) = +252.92; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.22 (s, 3H), 2.64 (d, J = 1.2 Hz, 1H), 5.59 (s, 1H), 5.64 (s, 1H), 6.80 (d, J = 8.4 Hz, 1H), 6.89 (q, J = 8.4, 23.6 Hz, 4H), 7.12 (m, 2H), 7.24 (m, 3H), 7.46 (s, 1H), 7.60 (d, J = 8.4 Hz, 1H), 7.87 ppm (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.9, 73.2, 117.2, 117.9, 123.4, 125.01, 125.05, 125.9, 126.4, 126.5, 126.8, 127.96, 128.03, 128.7, 129.0, 129.4, 129.6, 129.7, 130.1, 132.9, 133.3, 134.0, 136.7, 139.6, 141.7, 151.2 ppm; IR (KBr): $\tilde{\nu}$ = 3422, 3056, 2917, 1909, 1619, 1595, 1509, 1435, 1341, 1205, 1018 cm^{-1}.

Diol 7e: $[\alpha]_D^{25}$ (c = 1.18 in CH_2Cl_2) = +197.82; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.26 (dd, J = 2.8, 6.0 Hz, 1H), 5.31 (s, 1H), 5.76 (s, 1H), 6.77 (dd, J = 9.6, 18.0 Hz, 3H), 6.96 (q, J = 8.4 Hz, 2H), 7.13 (dd, J = 0.8, 8.4 Hz, 1H), 7.20 (d, J = 8.4 Hz, 1H), 7.32 (m, 2H), 7.51 (dd, J = 0.8, 7.6 Hz, 1H), 7.67 (d, J = 8.8 Hz, 1H), 7.93 ppm (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 72.8, 114.8, 115.0, 117.0, 117.8, 123.7, 124.7, 124.8, 126.4, 126.6, 126.7, 127.0, 127.8, 127.9, 128.09, 128.15, 129.1, 129.5, 129.8, 130.3, 133.0, 133.5, 133.9, 138.3, 141.5, 151.1 ppm; IR (KBr): $\tilde{\nu}$ = 3476, 3389, 3056, 2955, 1621, 1597, 1508, 1382, 1219, 1182, 1157, 1029 cm^{-1}.

Diol 7f: $[\alpha]_D^{25}$ (c = 1.96 in CH_2Cl_2) = +117.83; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.56 (s, 3H), 2.94 (d, J = 1.2 Hz, 1H), 5.82 (s, 1H), 6.24 (d, J = 1.6 Hz, 1H), 6.80 (d, J = 8.4 Hz, 1H), 6.86 (d, J = 7.6 Hz, 1H), 7.03–7.72 (m, 4H), 7.22 (m, 4H), 7.39 (d, J = 8.4 Hz, 1H), 7.45 (t, J = 7.2 Hz, 1H), 7.54 (d, J = 7.6 Hz, 1H), 7.85 ppm (dd, J = 8.4, 18.8 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.2, 71.4, 118.1, 118.5, 123.6, 124.8, 125.4, 125.9, 126.1, 126.2, 126.4, 126.5, 126.8, 127.2, 127.9, 128.1, 129.2, 129.4, 130.2, 131.5, 133.3, 133.6, 133.7, 135.1, 139.9, 140.1, 151.6 ppm; IR (KBr): $\tilde{\nu}$ = 3385, 3051, 1623, 1595, 1507, 1435, 1272, 1206, 1180, 1025 cm^{-1}.

Diol 7g: $[\alpha]_D^{25}$ (c = 0.68 in CH_2Cl_2) = +136.54; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.98 (s, 1H), 3.32 (s, 3H), 5.73 (m, 1H), 5.96 (s, 1H), 6.61 (d, J = 8.0 Hz, 1H), 6.88 (t, J = 8.8 Hz, 2H), 7.12 (m, 1H), 7.25 (m, 2H), 7.36 (t, J = 8.8 Hz, 2H), 7.44 (m, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.89 ppm (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.2, 71.4, 118.1, 118.5, 123.6, 124.8, 125.4, 125.9, 126.1, 126.2, 126.4, 126.5, 126.7, 127.3, 127.9, 128.1, 129.2, 129.3, 130.2, 131.5, 133.3, 133.5, 133.6, 135.1, 139.9, 140.0, 151.6 ppm; IR (KBr): $\tilde{\nu}$ = 3186, 3050, 2992, 2954, 2831, 1896, 1622, 1596, 1490, 1465, 1434, 1342, 1273, 1243, 1031 cm^{-1}.

Diol 7h: $[\alpha]_D^{25}$ (c = 1.0 in CH_2Cl_2) = +248.22; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.74–2.80 (m, 1H), 3.55 (s, 1H), 5.23 (s, CH_2Cl_2), 6.45 (s, 2H), 6.62 (q, J = 2.4, 8.0 Hz, 2H), 6.82 (d, J = 8.4 Hz, 1H), 7.01 (t, J = 8.0 Hz, 1H), 7.13 (q, J = 9.2, 18.0 Hz, 2H), 7.23–7.30 (m, 3H), 7.45 (t, J = 7.2 Hz, 1H), 7.58 (d, J = 8.8 Hz, 1H), 7.83–7.89 ppm (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.0, 73.2, 111.3, 113.1, 117.1, 118.0, 118.3, 123.5, 125.1, 126.47, 126.54, 126.6, 126.8, 128.08, 128.12, 129.1, 129.6, 130.0, 130.2, 133.0, 133.4, 134.2, 141.4, 144.3, 151.3, 159.3 ppm; IR (KBr): $\tilde{\nu}$ = 3394, 3056, 2927, 1596, 1490, 1434, 1259, 1206, 1144, 1029 cm^{-1}.

Diol 7k: $[\alpha]_D^{25}$ (c = 0.60 in CH_2Cl_2) = +263.58; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.20 (d, J = 1.2 Hz, 1H), 5.77 (s, 1H), 5.93 (s, 1H), 6.76 (d, J = 8.8 Hz, 1H), 6.99–7.05 (m, 2H), 7.16 (d, J = 8.4 Hz, 1H), 7.21–7.28 (m, 2H), 7.35 (t, J = 4.0 Hz, 3H), 7.42 (t, J = 8.0 Hz, 1H), 7.49 (t, J = 8.4 Hz, 2H), 7.55 (d, J = 8.8 Hz, 1H), 7.65 (t, J = 3.6 Hz, 1H), 7.78–7.87 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 73.4, 117.2, 118.0, 123.6, 124.3, 124.7, 125.0, 125.2, 125.6, 125.9, 126.55, 126.64, 126.9, 127.8, 128.0, 128.08, 128.12, 129.1, 129.6, 130.1, 130.3, 132.6, 132.97, 133.05, 133.4, 134.1, 139.9, 151.3 ppm; IR (KBr): $\tilde{\nu}$ = 3411, 3054, 2922, 1620, 1595, 1507, 1381, 1342, 1269, 1204, 1171, 1143, 1123, 1030 cm^{-1}.

Diol 7l: $[\alpha]_D^{25}$ (c = 0.50 in CH_2Cl_2) = +250.21; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.15 (s, 9H), 3.25 (s, 1H), 5.55 (s, 1H), 6.02 (s, 1H), 6.71 (d, J = 8.4 Hz, 1H), 6.82 (d, J = 8.0 Hz, 1H), 7.03 (t, J = 6.8 Hz, 1H), 7.11–7.26 (m, 7H), 7.42 (t, J = 6.8 Hz, 1H), 7.52 (d, J = 8.4 Hz, 1H), 7.78 ppm (t, J = 8.8 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 1.1, 73.3, 117.1, 118.0, 123.5, 125.1, 125.5, 126.4, 126.5, 126.6, 126.8, 128.0, 128.1, 129.1, 129.6, 130.05, 130.12, 133.0, 133.1, 133.4, 134.1, 139.0, 141.4, 143.9, 151.2 ppm; IR (KBr): $\tilde{\nu}$ = 3405, 3058, 2953, 1620, 1597, 1506, 1383, 1247, 1204, 1169, 1142, 1127, 1111, 1025 cm^{-1}.

Diol 7m: $[\alpha]_D^{25}$ (c = 1.63 in CH_2Cl_2) = +267.48; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.24 (s, 9H), 2.91 (s, 1H), 5.31 (s, CH_2Cl_2), 5.54 (s, 1H), 5.76 (s, 1H), 6.25 (d, J = 8.4 Hz, 1H), 6.83 (d, J = 8.4 Hz, 2H), 7.06 (t, J = 8.0 Hz, 3H), 7.19 (d, J = 8.4 Hz, 1H), 7.26–7.31 (m, 3H), 7.49 (t, J = 8.0 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.88 ppm (q, J = 8.8, 16.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.3, 34.4, 53.5 (CH_2Cl_2), 73.3, 117.1, 117.9, 123.5, 124.9, 124.97, 125.05, 125.9, 126.38, 126.44, 126.8, 127.9, 128.1, 129.0, 129.5, 129.7, 130.1, 133.1, 133.4, 134.0, 139.4, 141.7, 149.99, 151.1 ppm; IR (KBr): $\tilde{\nu}$ = 3404, 3058, 2960, 1618, 1595, 1507, 1459, 1383, 1362, 1267, 1205, 1169, 1142, 1026, 1011 cm^{-1}.

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