Asymmetric Radical Synthesis of 2,5-Diaryl-2,3-dihydrofurans − Application to the Preparation of (+)-Phyltetralin

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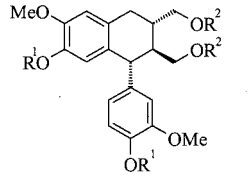
The diastereoselective Mn^{III}-promoted radical addition of β-oxo ester **1** onto *N*-cinnamoyloxazolidinone **2** affords, after removal of the chiral auxiliary, the enantiopure 2,5-diaryl-2,3-dihydrofuran (–)-**4**. Its $SnCl_4$-induced rearrangement leads to a 4-aryltetralone immediate precursor of the aryltetralin lignan (+)-phyltetralin (**9**).

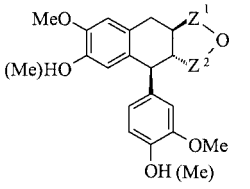
Introduction

Phyltetralin, an aryltetralin lignan, was first isolated from the leaves of *Phyllanthus niruri* L. (Euphorbiaceae).[1−3] *P. niruri* is one of the most widely used plants of the *Phyllanthus* genus in world folk medicine owing to its extensive distribution throughout many tropical and subtropical areas. It has been claimed to possess beneficial therapeutic effects against genitourinary infections, hepatitis B virus, and in the treatment of asthma and bronchial infections and it has a good reputation for its liver-protecting qualities.[4]

It was not until 1977 that Stevenson unambiguously established the structure and absolute configuration of phyltetralin by a semisynthesis starting from another, firmly known, aryltetralin lignan: simple manipulations performed on (−)-α-conidendrin led to the (−) enantiomer of the naturally occurring (+)-phyltetralin.[5] Two total syntheses of (±)-phyltetralin appeared shortly thereafter.[6,7] The first truly total synthesis of nonracemic phyltetralin was carried out by Meyers in 1988. It featured, as the key step, the conjugate addition of an aryllithium compound to a substituted naphthalene bearing a chiral oxazoline from which (+)-phyltetralin (68% *ee*) was obtained in five steps and 44% overall yield.[8] In addition, it should be noted that (−)-phyltetralin was formed as a minor compound (10%) by cyclization of the dibenzylbutane lignan (+)-phyllanthin.[9] Finally, a few syntheses of closely related compounds, namely α-conidendrin (dimethyl ether), α-retrodendrin (dimethyl ether) and isolariciresinol (dimethyl ether) have also been reported.[10−17]



R^1, R^2 = Me (+)-phyltetralin
R^1 = Me; R^2 = H (-)-isolariciresinol dimethyl ether
R^1, R^2 = H (-)-isolariciresinol



Z^1 = CO; Z^2 = CH_2 (-)-α-conidendrin (dimethyl ether)
Z^1 = CH_2; Z^2 = CO (-)-α-retrodendrin (dimethyl ether)

We describe here a short total synthesis of (+)-phyltetralin (100% *ee*) which constitutes the first realization of a strategy outlined by Fristad[18] in 1987 (but never validated since then, probably for want of a dependable method of obtaining the requisite enantiopure starting dihydrofurans) to prepare aryltetralin lignans (Scheme 1). It features, as the key step, the Lewis-acid-induced rearrangement of a 2,5-diaryl-2,3-dihydrofuran into a 4-aryltetralone possessing three contiguous stereogenic centers, followed by a few straightforward transformations. If applied to a (2*R*,3*R*)-2,5-diveratryl-2,3-dihydrofuran, this sequence could provide an easy access to (+)-phyltetralin.

Results and Discussion

We have previously reported that enantiopure functionalized *trans*-2,3-disubstituted 2,3-dihydrofurans can be prepared in good overall yield by the diastereoselective

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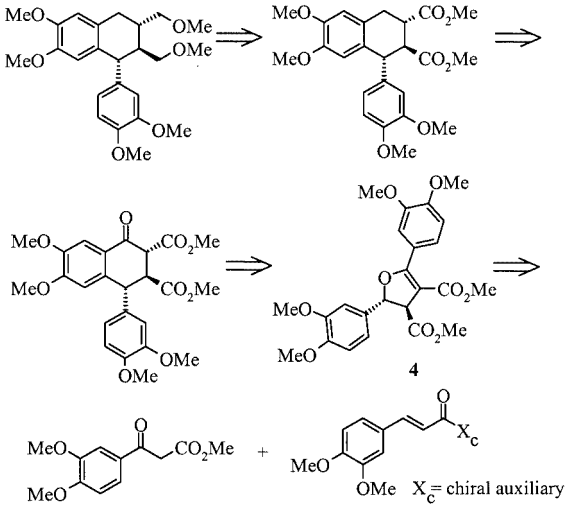


Scheme 1. Retrosynthetic analysis of (+)-phyltetralin

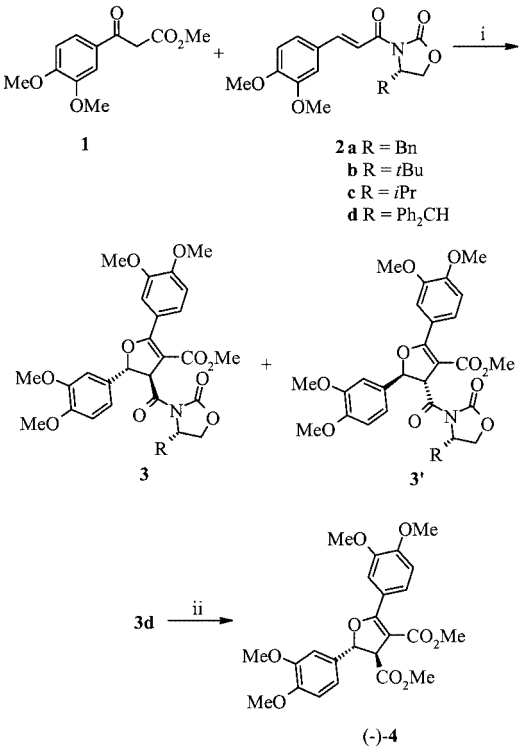
Mn^{III}-mediated radical addition of acetoacetic esters to chiral *N*-cinnamoyloxazolidinones,[19] separation of the major diastereomer, and cleavage of the chiral auxiliary. Furthermore, when using diverse (*S*)-4-substituted oxazolidinones, in each case the major dihydrofuran was shown to be (2*R*,3*R*).[20] Provided that this approach could be extended to the use of substituted benzoylacetic esters in terms of both yield and diastereoselectivity, we would have ready access to the required (2*R*,3*R*)-2,5-diveratryl-2,3-dihydrofuran **4** (Scheme 1).

A preliminary study conducted with benzoylacetate **1** and *N*-cinnamoyloxazolidinone **2a** demonstrated that this is indeed the case (Table 1 and Scheme 2). We then tested the three other oxazolidinones already employed in our previous work involving acetoacetates, in order to identify the chiral auxiliary able to ultimately furnish the maximum yield in pure isolated **4**.

Table 1. Addition of benzoylacetate **1** to **2a**−**d**

Substrate	R	Time [h]	Unchanged **2** (%)	**3** + **3′** (%)	**3**/**3′**
2a	Bn	3	11	73	65:35
2b	*t*Bu	3.5	10	73	84:16
2c	*i*Pr	2.5	13	70	79:21
2d	Ph_2CH	3	7	72	90:10

As can be seen for each entry, the oxidative addition of methyl 3,4-dimethoxybenzoylacetate (**1**)[21] to *N*-(3,4-dimethoxycinnamoyl)oxazolidinones **2a**−**d**[22] affords the two diastereomers **3** (major) and **3′** (minor) in good combined yield and with diastereoselectivities similar to those observed when using acetoacetates, with **2d** giving the best diastereomeric ratio. Accordingly, after condensing **1** onto **2d**, careful chromatography allowed us to obtain pure **3d**, which was then submitted to mild methanolysis to remove the chiral auxiliary,[23] furnishing (in 38% overall yield from **2d**) enantiopure (−)-**4**.

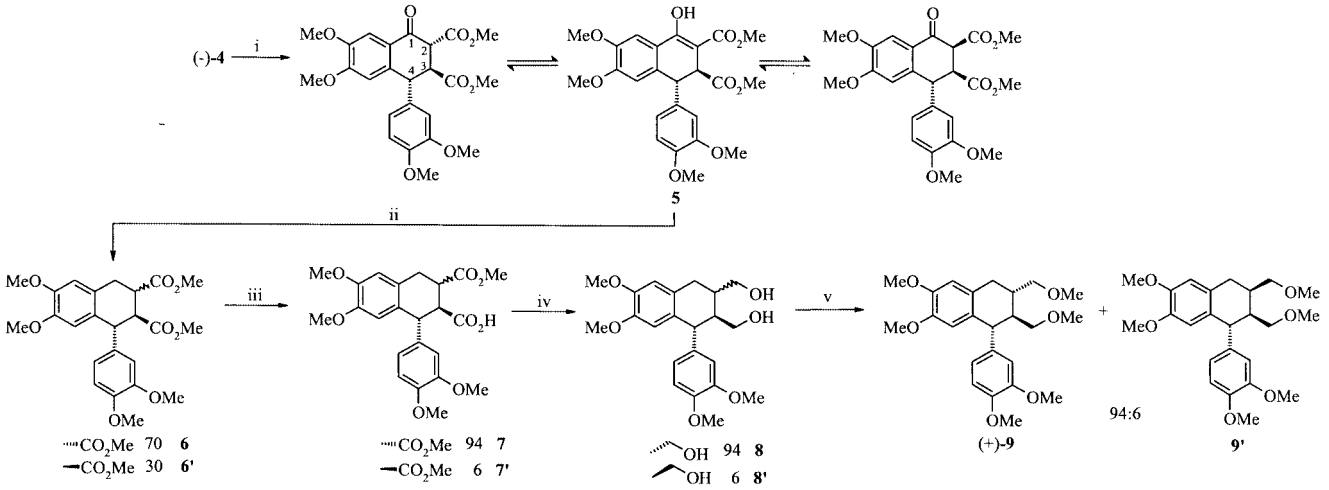


Scheme 2. Synthesis of enantiopure (−)-**4**; reaction conditions: (i) $Mn(OAc)_3 \cdot 2H_2O$, AcOH, 70 °C, N_2; (ii) LiBr, DBU, MeOH/THF, 0 °C, 3 h, 63%

Its absolute configuration was tentatively ascribed as (2*R*,3*R*) as we surmised that replacing acetoacetates by benzoylacetates in this reaction should not have altered its stereochemical course.

Having the chiron (−)-**4** in hand, the synthesis of (+)-phyltetralin was completed as shown in Scheme 3. The $SnCl_4$-induced rearrangement of (−)-**4** leads to the trisubstituted aryltetralone **5**, which exists in solution as an equilibrium mixture of the 2,3-*trans*, 2,3-*cis* and, mostly, enol forms.[24] **5** was then subjected to a reductive deoxygenation giving the epimeric aryltetralin diesters **6**/**6′** (2,3-*trans*/2,3-*cis*, 70:30). Treatment with MeONa/MeOH allowed us to raise this ratio to 94:6 in favor of the desired all-*trans* diastereomer with the concomitant (but not detrimental) transformation of the C-3 ester into the corresponding acid.[25] At this stage, the two isomers **7**/**7′** are inseparable. We therefore decided to treat the mixture with $LiAlH_4$, hoping to obtain a separation later.

Although the resulting diols (isolariciresinol dimethyl ether **8** and its C-2 epimer β-conidendrol dimethyl ether **8′**) could have been separated by crystallization,[14] we nonetheless preferred to transform the primary alcohols into their methyl ethers because we found that pure (+)-phyltetralin **9** could be easily isolated by silica-gel chromatography alongside its minor epimer β-conidendrol tetramethyl ether **9′**. With hindsight, we see that the formation of the (+)-enantiomer of phyltetralin validates our assumption that (−)-**4** actually possessed the (2*R*,3*R*) configuration depicted in Scheme 2.



Scheme 3. Synthesis of (+)-phyltetralin **9** from (−)-**4**; reaction conditions: (i) $SnCl_4$, CH_2Cl_2, r.t., 12 h, 93%; (ii) H_2, Pd/C, AcOH, 3 bar, 80 °C, 8 h, 73%; (iii) MeONa, MeOH, reflux, 24 h, 81%; (iv) $LiAlH_4$, THF, reflux, 30 min; (v) NaH, CH_3I, THF, r.t., 6 h, 74% over 2 steps

Conclusion

We have demonstrated that enantiopure (+)-phyltetralin can be prepared in five steps and 40% overall yield from a chiral 2,5-diaryl-2,3-dihydrofuran readily obtained by means of a short asymmetric radical synthesis. In conjunction with the development of more discriminative chiral auxiliaries (which we are currently investigating) this provides the basis of a general method to access a wide array of enantiopure aryltetralin lignans (natural and nonnatural) of predictable absolute configuration from easily available starting materials.

Experimental Section

General Remarks: All NMR spectra were recorded with a Bruker AC 250 spectrometer (^{1}H: 250 MHz; ^{13}C: 62 MHz). Chemical shifts are reported in ppm. The following abbreviations are used in reporting spectra: s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, dd = doublet of doublets, br. s = broad singlet. Infrared spectra were recorded with a Perkin−Elmer 297 spectrometer using thin-film deposition on NaCl plates, or in $CHCl_3$. Melting points were determined with an Electrothermal IA 9100 apparatus and are uncorrected. Optical rotations were measured with a Perkin−Elmer 241 polarimeter in a 1-dm cell.

Materials: All experiments were conducted under nitrogen unless indicated otherwise and the reaction mixtures stirred magnetically. $Mn(OAc)_3{\cdot}2H_2O$ was prepared from $Mn(OAc)_2{\cdot}4H_2O$ (Acros) according to a literature procedure.[26] $SnCl_4$ packaged under nitrogen (Aldrich) was used as received. Dichloromethane was distilled from P_2O_5, and THF from sodium benzophenone ketyl immediately prior to use. Flash chromatography was performed with Merck silica gel 60 H. Thin layer chromatography (TLC) was carried out on Merck silica-gel 60 F_{254} aluminum-backed plates. TLC visualization was done with a 254-nm UV lamp and phosphomolybdic acid staining solution.

General Procedure for the Oxidative Addition: *N*-Cinnamoyloxazolidinone **2** (1 mmol), methyl 3,4-dimethoxybenzoylacetate (**1**) (238 mg, 1 mmol) and $Mn(OAc)_3{\cdot}2H_2O$ (590 mg, 2.2 mmol) in AcOH (10 mL) were heated at 70 °C until complete discoloration. After cooling, H_2O (5 mL) was added and the mixture extracted with Et_2O (3 × 10 mL). The combined organic layers were washed with satd. aqueous $NaHCO_3$ and dried with $MgSO_4$. Evaporation of the solvent afforded the crude product which was purified by flash chromatography.

Dihydrofuran 3d: The above procedure was applied starting from **2d** (443 mg, 1 mmol). The crude product was purified by flash chromatography (hexane/Et_2O, from 9:1 to 1:1) to give first **3d** (414 mg, 0.61 mmol, 61% yield) then a mixture of **3d** and **3′d** (74 mg, 0.11 mmol, 11% yield). **3d:** M.p. 154−155 °C. $[\alpha]_D^{20}$ = −22.7 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.65 (s, 3 H), 3.90 (s, 3 H), 3.93 (s, 6 H), 3.95 (s, 3 H), 4.42−4.45 (m, 2 H), 4.72 (d, *J* = 6.7 Hz, 1 H), 5.28 (d, *J* = 6.6 Hz, 1 H), 5.48 (td, *J* = 3.1, 7.2 Hz, 1 H), 5.77 (d, *J* = 6.6 Hz, 1 H), 6.90 (m, 2 H), 6.93 (m, 2 H), 7.16−7.19 (m, 4 H), 7.25−7.33 (m, 6 H), 7.54−7.58 (m, 2 H) ppm. ^{13}C NMR (62 MHz, $CDCl_3$): δ = 51.22, 51.62, 53.68, 55.93, 55.96, 55.98, 56.00, 56.82, 65.47, 85.85, 101.70, 109.49, 110.09, 110.98, 112.82, 119.02, 121.48, 123.41, 127.17, 127.92, 128.46 (2 C), 128.69 (2 C), 129.03 (2 C), 129.25 (2 C), 131.20, 138.04, 139.31, 148.01, 149.13, 149.37, 151.36, 153.37, 164.69, 166.80, 173.11 ppm. IR ($CHCl_3$): ṽ = 3052, 2932, 1773, 1727, 1697, 1593, 1507, 1255, 1090 cm^{-1}. $C_{39}H_{37}NO_{10}$ (679.73): calcd. C 68.91, H 5.49, N 2.06, O 23.54; found C 68.58, H 5.54, N 2.00, O 23.88.

Dihydrofuran 4: LiBr (159 mg, 1.83 mmol) and DBU (0.11 mL, 0.73 mmol) were added to a cooled (0 °C) solution of **3d** (250 mg, 0.37 mmol) in MeOH (3 mL)/THF (1 mL). The stirring was continued at 0 °C until **3d** had been totally consumed (4 h). H_2O (5 mL) and Et_2O (5 mL) were then added. The aqueous layer was extracted with Et_2O (3 × 10 mL). The combined organic extracts were washed with 1 N aqueous HCl (3 × 5 mL) and H_2O (3 × 5 mL), and dried with $MgSO_4$. Evaporation of the solvent afforded the crude product which was purified by flash chromatography (hexane/Et_2O, from 9:1 to 1:1) to give **4** (105 mg, 0.23 mmol, 63% yield). M.p. 113 °C. $[\alpha]_D^{23}$ = −67.4 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.66 (s, 3 H), 3.78 (s, 3 H), 3.88 (s, 6 H), 3.93 (s, 6 H), 4.25 (d, *J* = 6.6 Hz, 1 H), 5.69 (d, *J* = 6.6 Hz, 1 H), 6.78−7.03 (m, 4 H), 7.62 (dd, *J* = 8.6, 1.3 Hz, 1 H), 7.68 (d, *J* = 1.3 Hz, 1 H) ppm. ^{13}C NMR (62 MHz, $CDCl_3$): δ = 51.22, 52.55, 55.91, 55.98, 56.03, 58.17, 58.26, 84.74, 100.47, 108.73, 110.20,

111.39, 112.97, 118.03, 121.37, 123.39, 132.52, 148.10, 149.42, 151.49, 164.82, 166.20, 173.32 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3051, 2985, 2952, 1730, 1600, 1507, 1261, 1090 cm^{-1}. $C_{24}H_{26}O_9$ (458.47): calcd. C 62.88, H 5.72, O 31.41; found C 62.73, H 5.88, O 31.39.

Aryltetralone 5: $SnCl_4$ (0.115 mL, 1 mmol) was added to a solution of (−)-**4** (46 mg, 0.10 mmol) in dry CH_2Cl_2 (2.5 mL) at room temperature. After **4** had been totally consumed (12 h), the reaction was quenched by slow addition of satd. aqueous $NaHCO_3$, diluted with an equal volume of H_2O, and extracted with Et_2O (3 × 5 mL). The combined organic layers were washed with satd. aqueous $NaHCO_3$ (5 × 5 mL) and H_2O (2 × 5 mL), and dried with $MgSO_4$. Evaporation of the solvent afforded the crude product which was purified by flash chromatography (hexane/EtOAc, from 9:1 to 1:1) to give **5** (43 mg, 0.09 mmol, 93% yield). **5 (Enol Form):** M.p. 133−134 °C. ^1H NMR (250 MHz, $CDCl_3$): δ = 3.66 (s, 3 H), 3.74 (s, 3 H), 3.81 (s, 3 H), 3.83 (s, 3 H), 3.86 (s, 3 H), 3.96 (s, 3 H), 4.54 (s, 1 H), 6.43 (dd, *J* = 7.2, 1.4 Hz, 1 H), 6.61 (br. s, 2 H), 6.68 (d, *J* = 7.2 Hz, 1 H), 7.44 (s, 1 H), 12.77 (br. s, 1 H) ppm. ^{13}C NMR (62 MHz, $CDCl_3$): δ = 45.12, 46.51, 51.96, 52.43, 55.83 (2 C), 56.01 (2 C), 107.18, 108.31, 110.82, 110.97, 111.44, 119.67, 132.50, 134.96, 139.35, 148.49, 148.55, 148.81, 151.79, 166.41, 169.43, 173.69 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3550−3000 (broad), 3050, 2992, 1739, 1513, 1420, 1261 cm^{-1}. $C_{24}H_{26}O_9$ (458.47): calcd. C 62.88, H 5.72, O 31.41; found C 63.06, H 5.55, O 31.39.

Aryltetralin Diesters 6/6′: A solution of **5** (150 mg, 0.33 mmol) in AcOH (7 mL) was introduced into a stainless steel reactor. 10% Pd on charcoal (166 mg) was then added. The mixture was placed under H_2 (3 bar) and heated at 80 °C for 8 h. After cooling, Pd was filtered through Celite and rinsed with Et_2O (3 × 10 mL). The filtrate was washed with satd. aqueous $NaHCO_3$ (5 × 5 mL) and dried with $MgSO_4$. Evaporation of the solvent afforded the crude product which was purified by flash chromatography (hexane/EtOAc, from 9:1 to 1:1) giving **6/6′** (106 mg, 0.24 mmol, 73% yield) as an inseparable mixture. Owing to peak overlaps between **6** and **6′** we only cite the ^1H signals unambiguously pertaining to **6** by comparison with the ^1H NMR spectrum of pure **6** already reported.[27] The ^{13}C NMR spectrum contains all the peaks pertaining to **6** by comparison with the ^{13}C NMR spectrum of pure **6** reported by Charlton[16] (these values are also consistent with those described by Nishizawa,[27] provided that all the chemical shifts cited therein are systematically incremented by + 1.0 ppm, in order to annul the discrepancy between them and those of Charlton). ^1H NMR (250 MHz, $CDCl_3$): δ = 3.47 (s, 3 H), 3.58 (s, 3 H), 3.69 (s, 3 H), 3.79 (s, 3 H), 3.87 (s, 3 H), 3.89 (s, 3 H), 4.18 (d, *J* = 10.9 Hz, 1 H) ppm. ^{13}C NMR (62 MHz, $CDCl_3$): δ = 31.83, 43.30, 48.83, 51.65, 51.72, 55.80, 55.87 (2 C), 55.94, 110.81, 110.99, 111.83, 112.21, 121.56, 126.12, 129.71, 135.48, 147.72, 147.81, 148.06, 149.03, 174.10, 174.58 ppm.

Aryltetralin Monoesters 7/7′: The purified mixture **6/6′** (44 mg, 0.10 mmol) and MeONa (38 mg, 0.70 mmol) were refluxed in MeOH (1 mL) for 24 h. After cooling, MeOH was evaporated and the solid residue taken up in H_2O (5 mL). After extraction with Et_2O (3 × 5 mL), the aqueous layer was acidified with 10% aqueous HCl and re-extracted with Et_2O (3 × 5 mL). The combined organic layers were then dried with $MgSO_4$. Evaporation of the solvent afforded **7/7′** (35 mg, 0.08 mmol, 81% yield) as an inseparable mixture, which was used in the next step without further purification. ^1H NMR (250 MHz, $CDCl_3$): δ = 2.91−3.34 (m, 4 H), 3.46 (s, 3 H), 3.59 (s, 3 H), 3.79 (s, 3 H), 3.86 (s, 3 H), 3.88 (s, 3 H), 4.13 (d, *J* = 10.6 Hz, 1 H), 6.20 (s, 1 H), 6.57 (d, *J* = 1.8 Hz, 1 H), 6.61 (s, 1 H), 6.67 (dd, *J* = 8.0, 1.8 Hz, 1 H), 6.78 (d, *J* = 8.0 Hz, 1 H) ppm. ^{13}C NMR (62 MHz, $CDCl_3$): δ = 31.81, 43.23, 49.01, 51.49, 51.86, 53.51, 55.85, 55.94, 55.99, 110.77, 110.96, 111.71, 112.12, 121.60, 125.91, 129.71, 135.26, 147.70, 147.85, 148.10, 149.06, 174.74, 179.42 ppm. IR (neat): $\tilde{\nu}$ = 3410−3051 (broad), 1732, 1640, 1633, 1507, 1420, 1261 cm^{-1}.

(+)-Phyltetralin (9): A solution of **7/7′** (35 mg, 0.08 mmol) in dry THF (2 mL) was added dropwise to a suspension of $LiAlH_4$ (61 mg, 1.62 mmol) in dry THF (3 mL). The reaction mixture was refluxed for 30 min. After cooling, H_2O (61 μL), 15% aqueous NaOH (61 μL), and H_2O (122 μL) were successively added. The resulting cloudy suspension was filtered through Celite which was then rinsed with CH_2Cl_2 (3 × 10 mL). The filtrate was concentrated to afford quantitatively the mixture **8/8′**, which was used in the next step without further purification. A suspension of oil-free NaH (4 mg, 0.08 mmol) in dry THF (5 mL) containing **8/8′** (32 mg, 0.08 mmol) was stirred at room temperature for 1 h. CH_3I (50 μL, 0.08 mmol) was added. After stirring for another 3 h, CH_3I (25 μL, 0.04 mmol) and oil-free NaH (4 mg, 0.08 mmol) were further added and the stirring continued for 2 h. The reaction mixture was cooled to 5 °C and quenched with H_2O (5 mL). The aqueous layer was extracted with Et_2O (3 × 5 mL). The combined organic extracts were washed with H_2O (3 × 4 mL) and dried with $MgSO_4$. Evaporation of the solvent afforded the crude product which was purified by flash chromatography (hexane/Et_2O, from 9:1 to 1:1) to give first phyltetralin **9** (25 mg, 0.06 mmol, 74% yield over two steps) then β-conidendrol tetramethyl ether **9′** (1 mg, 0.002 mmol). The enantiomeric purity of **9** can be checked by HPLC using a Daicel Amylose normal phase column CHIRALPAK® AD (hexane/2-propanol, 90:10, 1 mL/min). **9:** M.p. 98 °C. $[\alpha]_D^{23}$ = +7.0 (*c* = 0.8, $CHCl_3$).[28] ^1H NMR (250 MHz, $CDCl_3$): δ = 1.75−1.89 (m, 1 H), 2.10−2.24 (m, 1 H), 2.84 (d, *J* = 6.2 Hz, 2 H), 3.08 (dd, *J* = 9.4, 3.3 Hz, 1 H), 3.26 (s, 3 H), 3.36 (s, 3 H), 3.37 (dd, *J* = 9.4, 3.3 Hz, 1 H), 3.46 (m, 2 H), 3.58 (s, 3 H), 3.80 (s, 3 H), 3.84 (s, 3 H), 3.87 (s, 3 H), 3.99 (d, *J* = 10.3 Hz, 1 H), 6.22 (s, 1 H), 6.61 (s, 1 H), 6.62 (d, *J* = 1.7 Hz, 1 H), 6.70 (dd, *J* = 8.0, 1.7 Hz, 1 H), 6.81 (d, *J* = 8.0 Hz, 1 H) ppm. ^{13}C NMR (62 MHz, $CDCl_3$): δ = 33.20, 36.48, 45.02, 47.38, 55.95, 56.01, 56.05, 58.99, 59.06, 71.52, 75.48, 111.08, 111.25, 112.49, 113.05, 121.93, 129.02, 132.23, 138.18, 147.16, 147.30, 147.59, 149.04 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3045, 2972, 2932, 1513, 1480, 1420, 1260, 1130, 1102 cm^{-1}. $C_{24}H_{32}O_6$ (416.52): calcd. C 69.21, H 7.74, O 23.05; found C 69.37, H 7.80, O 22.83. **9′:** M.p. 115 °C. ^1H NMR (250 MHz, $CDCl_3$): δ = 2.16−2.42 (m, 2 H), 2.54 (dd, *J* = 16.1, 9.5 Hz, 1 H), 2.88 (dd, *J* = 16.1, 6.9 Hz, 1 H), 3.21−3.51 (m, 4 H), 3.27 (s, 3 H), 3.32 (s, 3 H), 3.69 (s, 3 H), 3.78 (s, 3 H), 3.82 (s, 3 H), 3.86 (s, 3 H), 4.09 (d, *J* = 4.0 Hz, 1 H), 6.38 (s, 1 H), 6.43 (dd, *J* = 7.9, 1.3 Hz, 1 H), 6.59 (d, *J* = 1.3 Hz, 1 H), 6.61 (s, 1 H), 6.71 (d, *J* = 7.9 Hz, 1 H) ppm. ^{13}C NMR (62 MHz, $CDCl_3$): δ = 30.02, 31.65, 43.71, 46.02, 55.92, 55.97, 56.06, 58.86, 58.99, 72.42, 75.14, 110.99, 111.44, 112.31, 113.64, 121.39, 128.11, 128.99, 139.36, 147.43, 147.61, 147.73, 148.90 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3043, 2975, 2932, 1520, 1480, 1418, 1260, 1130, 1110 cm^{-1}.

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