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An enantioselective synthesis of (*S*)- and (*R*)-curcuphenol

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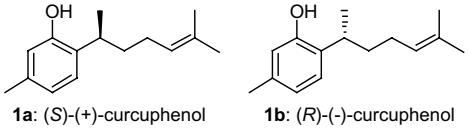
Abstract—The enantioselective synthesis of the phenolic sesquiterenses (*S*)- and (*R*)-curcuphenol is reported. The key step in this synthesis is the asymmetric conjugate addition using a readily available enantiomerically pure sulfoxide as the chiral auxiliary.

1. Introduction

(*S*)-(+)-Curcuphenol **1a**, which was isolated from the marine sponges *Didiscus flavus*, shows potent antifungal and antitumor activity,[1] while the (*R*)-(−)-curcuphenol **1b**, isolated from the gorgonian coral *Pseudopterogorgia rigida* shows antibacterial activity (Fig. 1).[2] Due to their diverse biological activities arise, some methods have been adapted to synthesize them,[3] such as enzymatic resolution of racemic intermediates,[3b] baker's yeast reduction,[3d,e] sparteine-mediated lateral metallation-substitution reaction,[3f] and intramolecular Michael addition reaction.[3g]



1a: (*S*)-(+)-curcuphenol **1b**: (*R*)-(-)-curcuphenol

Figure 1.

Herein, we report a new and effective synthetic route to both **1a** and **1b**, based on the asymmetric conjugate addition using an enantiomerically pure sulfoxide as the chiral auxiliary.[4–7]

2. Results and discussion

As shown in Scheme 1, the reaction of aldehyde **2** with (*R*)-(+)-methyl *p*-tolyl sulfoxide[8] in the presence of LDA followed by treatment of the mixture with excess sodium hydride and methyl iodide in one pot, afforded (*R*)-(+)-**3** in 78% yield.[9] Acid hydrolysis of (*R*)-(+)-**3** gave (*R*)-(+)-**4** in 95% yield. α-Lithiation followed by carboxylation and cyclization[10] produced enantiomerically pure (*S*)-(+)-3-(*p*-tolylsulfinyl)-7-methyl-2H-chromen-2-one **6** in 90% yield.

The key intermediate (*S*)-(+)-**6** was treated with 2 equiv of MeCuCNMgI at −78 °C, then sodium-amalgam reductive cleavage of the carbon–sulfur bond of the resultant conjugate adduct followed by $LiAlH_4$ reduction gave the expected (*S*)-**7a** in 50% yield (88% ee) over three steps (Scheme 2). However, in the absence of CuCN, mixed MeMgI[11] and (*S*)-(+)-**6** in THF at −78 °C ultimately gave (*R*)-methyl **7b** in 45% yield (74% ee) over three steps. Iodization of (*S*)-**7a** and (*R*)-**7b** afforded (*S*)-**8a** (in 98% yield) and (*R*)-**8b** (in 96% yield). The coupling of iodides **8a** and **8b** with Grignard reagent **9** catalyzed by Li_2CuCl_4 generated curcuphenol **1a** and **1b** in 40% and 41% yield, respectively.

Rationalization of these results involves two different transition states (Fig. 2).[11] Reaction of MeMgI with (*S*)-**6** at −78 °C via TS 1 led to the (*R*)-adduct. However, when adding cold (*S*)-**6** to MeCuCNMgI at −78 °C, the (*S*)-adduct was obtained probably because a metal ion chelate was formed first (TS 2).

3. Conclusion

In summary we report a facile route to asymmetric synthesis of **1a** and **1b**. The advantage of this method is that using one route can obtain **1a** and **1b**, respectively.

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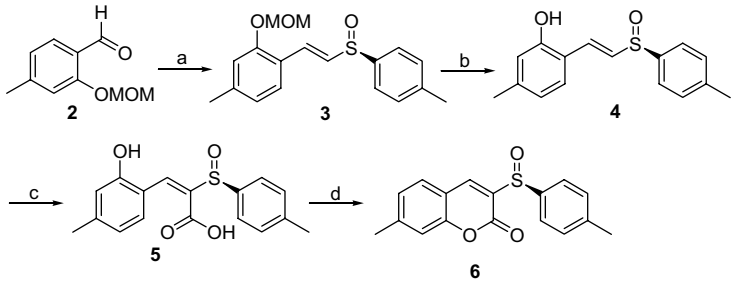
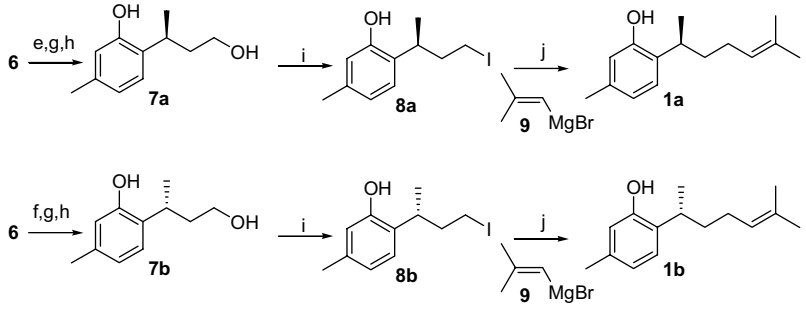


Scheme 1. Reagents and conditions: (a) 1.5 equiv LDA, (*R*)-1-methyl-4-(methylsulfinyl)benzene, THF, −78 °C, 30 min then excess of NaH and MeI, rt, 2 h, 78%; (b) 4-methylbenzenesulfonic acid, THF, reflux, 6 h, 95%; (c) 3 equiv LDA, CO_2, THF, −78 °C; (d) 4-methylbenzenesulfonic acid, $CHCl_3$, reflux, 20 min, 90% (two steps).



Scheme 2. Reagents and conditions: (e) MeCuCNMgI, THF, −78 °C; (f) MeMgI, THF, −78 °C; (g) Na_2HPO_4, Na(Hg), MeOH, rt; (h) $LiAlH_4$, THF, rt, **7a** (50%, over three steps), **7b** (45%, over three steps); (i) PPh_3, $C_3H_4N_2$, I_2, CH_2Cl_2, rt, **8a** (98%), **8b** (96%); (j) **9**, Li_2CuCl_4, THF, −40 to 0 °C, 24 h, **1a** (40%), **1b** (41%).

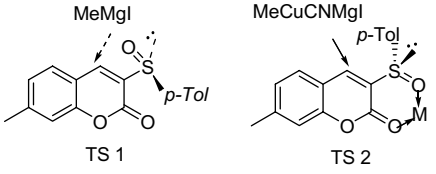


Figure 2.

4. Experimental

4.1. General

Melting points were measured on a Kofler apparatus and are uncorrected. The ^1H and ^{13}C NMR data were recorded in $CDCl_3$ solution with Bruker AM-200 or AM-300 spectrometer. The chemical shifts are reported in ppm relative to TMS. Optical rotations were determined on a JASCO J-20C polarimeter with a 0.2 dm tube. Mass spectra were measured with an EI (70 eV) technique. Chiral analysis was performed on Varian Dynamax SD-300 using (chiralcel) column CDMPC (150 × 4.6 mm ϕ) with hexane/isopropyl alcohol as eluent. Column chromatographs were generally performed on silica gel (200–300 mesh) eluting with petroleum ether/ethyl acetate or chloroform/ethyl acetate.

4.2. 1-((*R*)-(*E*)-2-(*p*-Tolylsulfinyl)vinyl)-2-(methoxymethoxy)-4-methylbenzene, 3

To a solution of 2-hydroxy-4-methylbenzaldehyde **2** (2.72 g, 20.00 mmol) in dry THF (50 mL) was added 60% NaH (0.84 g, 21.00 mmol). The mixture was stirred for 10 min and then methoxymethyl chloride (1.54 mL, 20 mmol) was added slowly via syringe. The reaction mixture was stirred for 15 min and used directly in the next step.

To a cold (−78 °C) 30 mmol THF solution of 1.5 equiv of LDA, previously formed at 0 °C, was added under argon 1 equiv of (*R*)-(+)-methyl *p*-tolyl sulfoxide (3.08 g, 20 mmol) in THF (3 mL/mmol). After stirring for 15 min, the above solution **2** in THF was slowly added via pressure-equalizing dropping funnel. The mixture was treated with excess of MeI after warmed up to room temperature, and then with excess of NaH. The reaction mixture was quenched after 2 h of stirring with a saturated NH_4Cl solution. The aqueous phase was extracted with Et_2O (3 × 50 mL). The combined organic extracts were washed with a saturated NaCl solution, dried over anhydrous Na_2SO_4 and the solvent evaporated in vacuo. The crude products were purified by column chromatography using petroleum ether and acetate (4:1, v/v) to afford (*R*)-**3** (4.93 g, 78%), $[\alpha]_D^{25} = +59$ (*c* 2.56, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ 2.27 (s, 3H), 2.33 (s, 3H), 3.41 (s, 3H), 5.17 (s, 2H), 6.73 (d, 1H, J = 7.6 Hz), 6.85 (d, 1H, J = 15.8 Hz), 6.91 (s, 1H), 7.27 (d, 3H, J = 7.6 Hz), 7.53 (d, 2H, J = 7.6 Hz), 7.60 (d, 1H, J = 15.8 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.1, 21.4, 56.0, 94.2, 115.1, 120.3, 122.5, 124.5, 128.3, 129.7, 131.9, 132.6, 141.1, 141.5, 155.3. MS (EI): *m*/*z* 316 (M^+, 1), 300 (3), 268 (23), 255 (4), 223 (13), 195 (6), 163 (5), 139 (6), 132 (19), 123 (12), 91 (7), 77 (9),

45 (100). Anal. Calcd for $C_{18}H_{20}O_3S$: C, 68.33; H, 6.37; S, 10.13. Found: C, 68.21; H, 6.43; S, 10.30.

4.3. 2-(*R*)-(*E*)-2-(*p*-Tolylsulfinyl)vinyl-5-methylphenol, 4

To a solution of (*R*)-**3** (4.9 g, 15.5 mmol) in THF (60 mL) was added 4-methylbenzenesulfonic acid (3 mmol). The mixture was heated under refluxing for 6 h. After being cooled, the solution was poured into water (10 mL) and neutralized with Na_2CO_3 to pH 7–8. The aqueous phase was extracted with EtOAc (3×40 mL). The combined organic extracts were washed with a saturated NaCl solution, dried over anhydrous Na_2SO_4, and the solvent was evaporated in vacuo. The crude products were purified by column chromatography using $CHCl_3$ and EtOAc (10:1, v/v) to afford (*R*)-**4** (4.0 g, 95%) as a white solid. Mp 172–174 °C, $[\alpha]_D^{25} = +187$ (*c* 0.40, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.24 (s, 3H), 2.39 (s, 3H), 6.63 (d, 1H, $J = 7.8$ Hz), 6.76 (s, 1H), 7.13 (d, 1H, $J = 7.8$ Hz), 7.27 (d, 2H, $J = 7.5$ Hz), 7.40 (s, 2H), 7.57 (d, 2H, $J = 7.5$ Hz), 9.18 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.7, 116.7, 117.1, 120.0, 124.3, 129.3, 130.2, 130.7, 136.0, 139.6, 140.8, 141.4, 156.2. FAB: M+1, 273.1. MS (EI): *m*/*z* 256 (23), 224 (38), 179 (10), 165 (8), 135 (100), 121 (34), 105 (55), 91 (87), 77 (70), 65 (46), 45 (34), 39 (38). Anal. Calcd for $C_{16}H_{16}O_2S$: C, 70.56; H, 5.92; S, 11.77. Found: C, 70.41; H, 5.80; S, 11.95.

4.4. (*S*)-2-(*p*-Tolylsulfinyl)-3-(2-hydroxy-4-methylphenyl)acrylic acid, 5

To a cold (−78 °C) 42 mmol THF solution of 3.0 equiv of LDA, previously formed at 0 °C, was added under argon 1 equiv of (*R*)-**4** (3.81 g, 14.0 mmol) in THF (5 mL/mmol). After stirring for 15 min, excess of solid dry ice was added in portion. The reaction mixture was allowed to warm up to room temperature over 2 h after which time water was added. The aqueous layer was acidified with 6 M HCl pH 2–3 and then extracted with Et_2O (3×50 mL). The combined organic extracts were washed with a saturated NaCl solution, dried over anhydrous Na_2SO_4, and the solvent evaporated in vacuo. The acid **5** was used directly in the next step.

4.5. (*S*)-(+)-3-(*p*-Tolylsulfinyl)-7-methyl-2*H*-chromen-2-one, 6

The above crude product was dissolved in $CHCl_3$ (50 mL), and treated with 4-methylbenzenesulfonic acid (1.0 mmol). The mixture was heated under refluxing for 20 min. After being cooled, the solution was poured into water (10 mL) and neutralized with Na_2CO_3. The aqueous phase was extracted with $CHCl_3$ (3×40 mL). The combined organic extracts were washed with a saturated NaCl solution, dried over anhydrous Na_2SO_4, and the solvent was evaporated in vacuo. The crude products were purified by column chromatography using chloroform and ethyl acetate (50:1, v/v) to afford (*S*)-**6** (3.75 g, 90%) as white solid. Mp 219–220 °C, $[\alpha]_D^{22} = +18$ (*c* 2.00, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.35 (s, 3H), 2.45 (s, 3H), 7.12 (s, 1H), 7.15 (d, 1H, $J = 7.8$ Hz), 7.26 (d, 2H, $J = 7.5$ Hz), 7.52 (d, 1H, $J = 7.8$ Hz), 7.72 (d, 2H, $J = 7.5$ Hz), 8.42 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.4, 21.9, 116.1, 116.9, 125.6, 126.3, 128.6, 129.9, 132.7, 139.4, 139.7, 142.5, 144.9, 154.1, 157.0. MS (EI): *m*/*z* 298 (M^+, 25), 282 (4), 250 (100), 222 (29), 187 (10), 163 (17), 147 (27), 91 (30), 77 (42), 43 (58). Anal. Calcd for $C_{17}H_{14}O_3S$: C, 68.44; H, 4.73; S, 10.75. Found: C, 68.50; H, 4.80; S, 10.61.

4.6. 2-((*S*)-4-Hydroxybutan-2-yl)-5-methylphenol, 7a

To a cold (−78 °C) solution of the organocuprate reagent [formed from 2 equiv CuCN and 2 equiv of MeMgI (1.4 M in THF)] in THF (10 mL) was added dropwise (*S*)-**6** (0.596 g, 2.0 mmol) in THF (40 mL) under argon with vigorous stirring. After 30 min at −78 °C, the reaction mixture was allowed to warm up to room temperature over 30 min after which time a saturated NH_4Cl solution was added. The aqueous layer was extracted with ether (3×20 mL), and the combined organic extracts were washed with a saturated solution of $Na_2S_2O_3$ and brine. After quickly drying over $MgSO_4$ and concentration under reduced pressure, the crude conjugate adduct was used directly in the next step.

The above crude conjugate adduct was dissolved in dry MeOH (40 mL), cooled to 0 °C, and treated with Na_2HPO_4 (1.99 g, 15.0 mmol) and Na(Hg) (7.73 g, 20.0 mmol). After 2 h of vigorous stirring at 0 °C, the reaction mixture was quenched with a saturated NH_4Cl solution. The product was extracted into ether, dried with anhydrous Na_2SO_4, concentrated under reduced pressure. The product was used directly in the next step.

The above crude product was dissolved in dry THF, and treated with $LiAlH_4$ (76 mg, 2.0 mmol). The reaction mixture was stirred at room temperature for 1 h. The reaction mixture was quenched first with wet diethyl ether and then with dil. aq HCl. It was then extracted with diethyl ether (3×12 mL) and the combined organic extracts were washed successively with a saturated solution of $NaHCO_3$ and NaCl, dried over anhydrous Na_2SO_4, and the solvent was evaporated in vacuo. The crude products were purified by column chromatography using petroleum ether and acetate (4:1, v/v) to afford (*S*)-**7a** (180 mg, 50%) as a colorless oil. $[\alpha]_D^{15} = +23$ (*c* 1.30, $CHCl_3$, ee 88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.32 (d, 3H, $J = 7.2$ Hz), 1.49–1.59 (m, 1H), 1.94–2.07 (m, 1H), 2.30 (s, 3H), 3.30–3.42 (m, 2H), 3.65–3.69 (m, 1H), 6.67 (s, 1H), 6.75 (d, 1H, $J = 7.8$ Hz), 7.06 (d, 1H, $J = 7.8$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.9, 26.7, 40.8, 60.7, 116.6, 121.8, 126.5, 128.8, 136.9, 153.6. MS (EI): *m*/*z* 180 (M^+, 16), 162 (2), 147 (19), 135 (100), 121 (11), 115 (16), 91 (40), 77 (30), 65 (12), 51 (16). Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.41; H, 9.01.

4.7. 2-((*R*)-4-Hydroxybutan-2-yl)-5-methylphenol, 7b

Following the above procedure, (*R*)-**7b** was obtained from MeMgI as the conjugate reagent in the absence of CuCN. The overall chemical yield over three steps was 45%, 162 mg, ee 74%, $[\alpha]_D^{15} = -19$ (*c* 1.32, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.31 (d, 3H,

J = 7.2 Hz), 1.48–1.56 (m, 1H), 1.93–2.07 (m, 1H), 2.29 (s, 3H), 3.31–3.42 (m, 2H), 3.62–3.68 (m, 1H), 6.67 (s, 1H), 6.75 (d, 1H, J = 7.8 Hz), 7.06 (d, 1H, J = 7.8). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.9, 26.7, 40.8, 60.7, 116.6, 121.8, 126.4, 128.8, 136.9, 153.6. MS (EI): m/z 180 (M^+, 16), 162 (2), 147 (18), 135 (100), 121 (11), 115 (17), 91 (40), 77 (31), 65 (12), 51 (16). Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.47; H, 8.87.

4.8. 2-((*S*)-4-Iodobutan-2-yl)-5-methylphenol, 8a

Alcohol (*S*)-**7a** (180 mg, 2.0 mmol) as a solution in dry CH_2Cl_2 (5 mL), was cooled to 0 °C and treated under argon with PPh_3 (629 mg, 2.4 mmol), imidazole [$C_3H_4N_2$ (163 mg, 2.4 mmol)], I_2 (610 mg, 2.4 mmol). After 2 h of vigorous stirring at 0 °C, the reaction mixture was quenched with a 2 M $Na_2S_2O_3$ solution (5 mL). The product was extracted into ether, dried over Na_2SO_4, concentrated under reduced pressure. The latter was purified by chromatography with petroleum ether and acetate (95:5, v/v) to afford (*S*)-**8a** (284 mg, 98%) as a colorless oil. $[\alpha]_D^{15} = +36$ (c 1.25, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.26 (d, 3H, J = 7.2 Hz), 2.05–2.25 (m, 2H), 2.28 (s, 3H), 3.04–3.21 (m, 3H), 4.76 (b, 1H), 6.58 (s, 1H), 6.73 (d, 1H, J = 7.8 Hz), 7.03 (d, 1H, J = 7.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 5.5, 20.3, 20.9, 33.6, 40.8, 116.4, 121.9, 127.3, 128.0, 137.1, 152.9. MS (EI): m/z 290 (M^+, 15), 163 (0.4), 162 (0.4), 147 (4), 135 (100), 121 (8), 107 (6), 91 (19), 77 (8), 65 (3), 51 (3), 39 (5). Anal. Calcd for $C_{11}H_{15}OI$: C, 45.54; H, 5.21. Found: C, 45.44; H, 5.09.

4.9. 2-((*R*)-4-Iodobutan-2-yl)-5-methylphenol, 8b

Following the above procedure, (*R*)-**8b** was obtained from (*R*)-**7b** (162 mg) in 96% chemical yield (251 mg), $[\alpha]_D^{15} = -31$ (c 1.50, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.26 (d, 3H, J = 7.2 Hz), 2.02–2.25 (m, 2H), 2.28 (s, 3H), 3.04–3.20 (m, 3H), 4.67 (b, 1H), 6.58 (s, 1H), 6.73 (d, 1H, J = 7.8 Hz), 7.02 (d, 1H, J = 7.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 5.5, 20.3, 20.9, 33.6, 40.8, 116.4, 121.9, 127.3, 128.0, 137.1, 152.9. MS (EI): m/z 290 (M^+, 15), 163 (0.4), 162 (0.4), 147 (4), 135 (100), 121 (8), 107 (6), 91 (20), 77(8), 65 (3), 51 (3), 39 (5). Anal. Calcd for $C_{11}H_{15}OI$: C, 45.54; H, 5.21. Found: C, 45.38; H, 5.34.

4.10. (*S*)-(+)-Curcuphenol, 1a

Iodide (*S*)-**8a** (261 mg, 0.9 mmol) as a solution in dry THF (2 mL) was cooled to −40 °C and treated under argon with Li_2CuCl_4 (0.18 mmol) and Grignard **9** (3.6 mmol, 0.5 M in THF). The reaction mixture was allowed to warm to 0 °C and stirred at this temperature for 24 h. Work-up with a saturated NH_4Cl solution, extraction with diethyl ether, and concentration of the dried over Na_2SO_4 organic phase gave the crude product. This was purified by chromatography with petroleum ether and acetate (95:5, v/v) to afford (*S*)-(+)-curcuphenol **1a** (78 mg, 40%) as colorless oil. $[\alpha]_D^{15} = +21$ (c 1.50, $CHCl_3$), (Lit.[1] $[\alpha]_D = +24.6 \pm 2$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.25 (d, 3H, J = 6.9 Hz), 1.50–1.76 (m, 2H), 1.56 (s, 3H), 1.70 (s, 3H), 1.92–1.99 (m, 2H), 2.29 (s, 3H), 2.93–3.05 (m, 1 H), 4.73 (s, 1H), 5.15 (t, 1H, J = 6.9 Hz), 6.60 (s, 1H), 6.74 (d, 1H, J = 7.8 Hz), 7.05 (d, 1H, J = 7.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.7, 20.9, 21.1, 25.7, 26.0, 31.3, 37.2, 116.1, 121.7, 124.6, 126.8, 129.9, 132.0, 136.5, 152.8. MS (EI): m/z 218 (M^+, 16), 203 (1), 175 (1), 161 (7), 148 (32), 135 (100), 121 (21), 107 (5),91 (20), 77 (7), 69 (7), 55 (7), 41(13). Anal. Calcd for $C_{15}H_{22}O$: C, 82.52; H, 10.16. Found: C, 82.61; H, 10.10.

4.11. (*R*)-(−)-Curcuphenol, 1b

Following the above procedure, (*R*)-**1b** was obtained from (*R*)-**8b** (240 mg) in 41% chemical yield (74 mg), $[\alpha]_D^{15} = -18$ (c 2.50, $CHCl_3$) (Lit.[1] *ent*-**1b** $[\alpha]_D$ = +24.6 ± 2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.25 (d, 3H, J = 6.9 Hz), 1.49–1.75 (m, 2H), 1.56 (s, 3H), 1.70 (s, 3H), 1.93–1.99 (m, 2H), 2.29 (s, 3H), 2.94–3.06 (m, 1 H), 4.74 (s, 1H), 5.15 (t, 1H, J = 6.9 Hz), 6.60 (s, 1H), 6.74 (d, 1H, J = 7.8 Hz), 7.05 (d, 1H, J = 7.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.7, 20.9, 21.1, 25.7, 26.1, 31.4, 37.3, 116.1, 121.7, 124.6, 126.8, 129.9, 132.0, 136.5, 152.8. MS (EI): m/z 218 (M^+, 16), 203 (1), 175 (1), 161 (7), 148 (32), 135 (100), 121 (21), 107 (5),91 (20), 77 (7), 69 (7), 55 (7), 41(13). Anal. Calcd for $C_{15}H_{22}O$: C, 82.52; H, 10.16. Found: C, 82.39; H, 10.00.

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References

1. Wright, A.; Pomponi, S.; McConnel, O. J.; Komoto, S.; McCarthy, P. J. *J. Nat. Prod.* **1987**, *50*, 976–978.
2. McEnroe, F. J.; Fenical, W. *Tetrahedron* **1978**, *34*, 1661–1664.
3. (a) Ghisalberti, E. L.; Jefferies, P. R.; Stuart, A. D. *Aust. J. Chem.* **1979**, *32*, 1627; (b) Ono, M.; Oguta, Y.; Hatogai, K.; Akita, H. *Tetrahedron: Asymmetry* **1995**, *6*, 1829; (c) Sugahara, T.; Ogasawara, K. *Tetrahedron: Asymmetry* **1998**, *9*, 2215–2217; (d) Fuganti, C.; Serra, S. *Synlett* **1998**, 1252; (e) Fuganti, C.; Serra, S. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3758–3764; (f) Kimachi, T.; Takemoto, Y. *J. Org. Chem.* **2001**, *66*, 2700; (g) Harmata, M.; Hong, X.; Barnes, C. L. *Tetrahedron Lett.* **2003**, *44*, 7261–7264.
4. Posner, G. H. *Acc. Chem. Res.* **1987**, *20*, 72–79.
5. Posner, G. H.; Hulce, M. *Tetrahedron Lett.* **1984**, *25*, 379–382.
6. Posner, G. H.; Kogan, T. P.; Hulce, M. *Tetrahedron Lett.* **1984**, *25*, 383–386.
7. Posner, G. H.; Kogan, T. P.; Haines, S. R.; Frye, L. L. *Tetrahedron Lett.* **1984**, *25*, 2627.
8. Solladié, G.; Hutt, J.; Girardin, A. *Synthesis* **1987**, 173.
9. Tsuchihashi, G.; Mitamura, S.; Inoue, S.; Ogura, K. *Tetrahedron Lett.* **1973**, *4*, 323–326.
10. Posner, G. H.; Weitzberg, M.; Hamill, T. G.; Asirvatham, E.; Cun-Heng, H.; Clardy, J. *Tetrahedron* **1986**, *42*, 2919.
11. Posner, G. H.; Mallamo, J. P.; Hulce, M.; Frye, L. L. *J. Am. Chem. Soc.* **1982**, *104*, 4180–4185.