Synthesis of the structure proposed for the natural allenic antibiotic scorodonin†

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The structure proposed for scorodonin, a natural allenyne with significant antibacterial and antifungal activities, was synthesized through an enantioselective route. The spectroscopic data of the synthetic allenyne are generally consistent with those reported for the natural one, but slight yet definite differences were observed in ^{13}C NMR.

Introduction

Scorodonin (with the structure proposed as **1**, Fig. 1) is a member of the rare group of natural C7-acetylenes isolated from *Marasmius scorodonius*,[1a] with inhibiting effects on the growth of bacteria, yeasts and filamentous fungi. It also has an inhibiting effect on the incorporation of thymidine and uridine into DNA and RNA in cells of the ascitic form of Ehrlich carcinoma. The structure of scorodonin was established mainly by spectroscopic means with the presence of chloride and the C-7 linear backbone confirmed *via* chemical reactions.

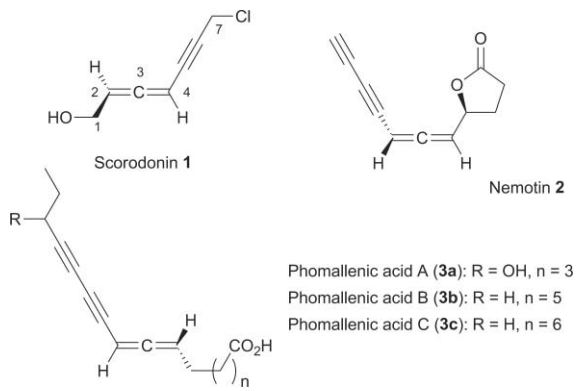
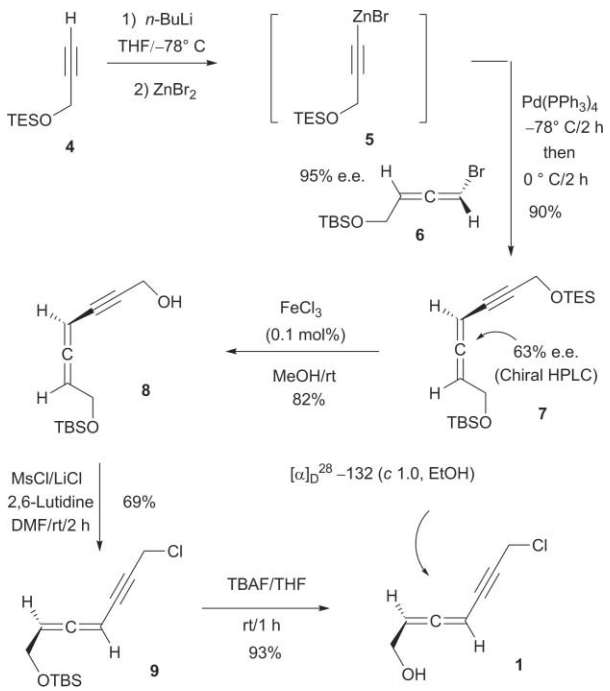


Fig. 1 The proposed structure for scorodonin (**1**) and the structures for nemotin (**2**) and phomallenic acids (**3a–c**).

Structurally similar compounds with potent antibacterial activity are also known, including nemotin[2] (**2**) and phomallenic acids[3] (**3**). The latter have been shown to be new inhibitors of FabF, an essential enzyme in bacterial type II fatty acid synthesis pathway (FAS II).[4] As part of our work on allenic natural products, we also performed an enantioselective synthesis of **1**. Herein we wish to detail the results of this work.

Results and discussion

Our synthesis is shown in Scheme 1, which emerged with a coupling of alkyne **4** with bromoallene **6**. Construction of the optically active **6** was recently disclosed.[5] Treatment of **6** with **5** prepared *in situ* from **4** *via* deprotonation with *n*-BuLi followed by metal exchange with anhydrous $ZnBr_2$ gave allenyne **7** in 90% yield. The configuration of the allene axis was inverted during the process as noted earlier by Elsevier and Vermeer.[6]



Scheme 1 Synthesis of the proposed structure of scorodonin (**1**).

The TES (triethylsilyl) protecting group was selectively cleaved using the conditions (a catalytic amount of $FeCl_3$ in MeOH) developed[7] earlier in our laboratory, affording the propargyl alcohol **8**. Further treatment of this alcohol with MsCl and LiCl in DMF (*N*,*N*-dimethylformamide) in the presence of 2,6-lutidine at ambient temperature for 2 h led to the corresponding chloride

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Table 1 Comparison of ^{1}H and ^{13}C NMR data for the natural (ref. 1) and synthetic **1** (this work)

^{1}H NMR ($CDCl_3$) δ (ppm)		^{13}C NMR (acetone-d_6) δ (ppm)	
Natural (90 MHz)	Synthetic (300 MHz)	Natural (20.1 MHz)	Synthetic (75 MHz)
4.20, OH	1.79 (br s, 1 H, OH)	58.1 (C-1)	59.53
4.22 (dd, *J* 5.6, 3.2 Hz, 2H)	4.21 (dd, *J* 3.0, 6.0 Hz, 2H)	95.5 (C-2)	95.57
4.27 (dd, *J* 2.2, 1.2 Hz, 2H)	4.26 (dd, *J* 0.9, 2.4 Hz, 2H)	210.0 (C-3)	212.57
5.61 (dtt, *J* 6.6, 3.2, 2.2 Hz, 1H)	5.60–5.53 (m, 1H)	76.0 (C-4)	76.50
5.69 (dtt, *J* 6.6, 5.6, 1.2 Hz, 1H)	5.66 (dtt, *J* 6.4, 6.2, 1.1 Hz,1H)	85.8 (C-5)	85.69
		79.6 (C-6)	79.79
		31.5 (C-7)	31.75

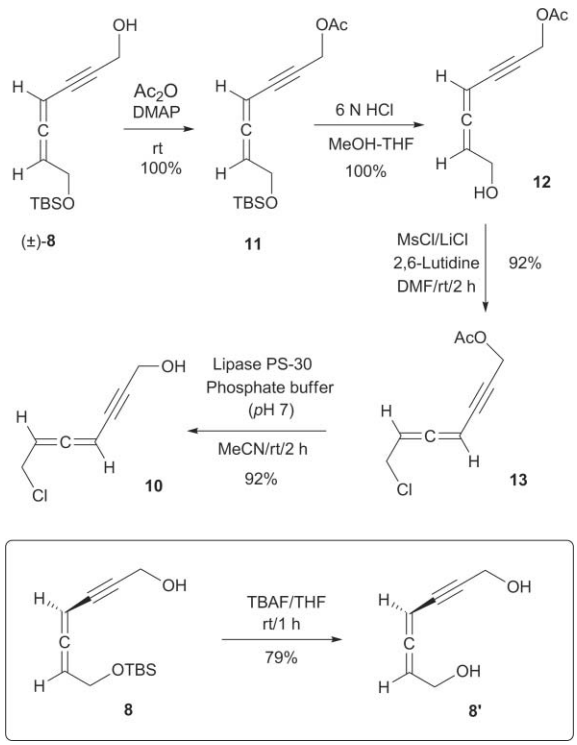
9. Finally, removal of the TBS (*tert*-butyldimethylsilyl) protecting group resulted in the end product **1** in 93% yield.‡

The ^{1}H NMR data of our synthetic **1** were in excellent consistency with those reported for the natural scorodonin (Table 1). However, small yet distinct differences were observed for the C-1 and C-3 between the two sets of ^{13}C NMR data. In a recent study on another natural product (penipratynolene) we had already encountered seemingly similar problems of inconsistence of NMR data caused by erroneous report of the NMR solvent employed.[8] To find out if it was also the case here with scorodonin, we recorded ^{13}C NMR of synthetic **1** in $CDCl_3$, the same solvent for the ^{1}H NMR measurements in both studies. The results are unambiguous, with essentially no single signal (*cf.* Experimental) close to its counterpart in the spectrum recorded in acetone-d_6. Thus, the ^{13}C NMR shifts discrepancies are not caused by use of different solvents.

Another possibility is that scorodonin has an OH–Cl switched structure (**10**). Such a functionality arrangement was excluded in the original[1] structure determination mainly on the basis of empirical rules of chemical shifts. However, as the previous almost impeccable assignment of a linear C7 backbone with a conjugated allene-yne and a primary alcohol/primary chloride left essentially no other alternatives, to be on the safe side it would be good to actually measure the NMR of compound **10**. For this reason, we next synthesized this compound.§

As depicted in Scheme 2, the propargylic OH in **8** was acetylated with AcO in the presence of DMAP (4-*N*-dimethylaminopyridine). For convenience, a racemic substrate was utilized here. The TBS protecting group was then cleaved with 6 N HCl, releasing a free hydroxyl group for chlorination. Further treatment of **12** with MsCl/LiCl/2,6-lutidine in DMF gave **13** in 92% yield. Finally, the acetyl group was hydrolyzed with the aid of lipase PS-30,[9] delivering the desired **10** in 92% yield.

The ^{1}H and ^{13}C NMR of **10** were then measured in $CDCl_3$ and acetone-d_6, respectively, for comparison with the literature data. Because these data (*cf.* Experimental) are completely incompatible with those reported for the natural scorodonin, **10** can be reliably/experimentally excluded as the structure for natural scorodonin.



Scheme 2 Synthesis of two analogues of **1**.

Then we noticed that the allenynol **1** contains an activated chloride, which like other propargyl chlorides tend to hydrolyze under certain conditions. If the natural **1** were unexpectedly hydrolyzed before the ^{13}C NMR was taken, the recorded spectrum would be that of **8′**. To exclude this (hypothetic) possibility, we prepared compound **8′** from **8** and measured its NMR. Again, neither ^{1}H nor ^{13}C NMR data can match their counterpart for the natural scorodonin. As all the above mentioned possibilities have been excluded, the originally proposed structure (**1**) remains as the most likely correct one though before a final conclusion is reached the *ca.* 2 ppm differences in the ^{13}C signals still need to be addressed.¶

‡ The low polarity and instability of **9** and **1** made it unfeasible to perform direct measurement of their e.e. values by chiral HPLC.

§ Because for molecules of only one chiral element the NMR spectra for racemic and enantiopure sample are the same, racemic **8** was employed in the synthesis of **10** to minimize the workload.

¶ Re-recording of ^{13}C spectrum for the natural scorodonin on a modern NMR instrument may clear all doubts about the discrepancy. However, this is unfeasible because we do not have any access to the natural sample. For the time being, the most possible explanation seems to be a data reporting/reading error in the previous work. Given the relatively low resolution/frequency of the NMR instruments back in the 1970 s, such errors might be more likely to occur than nowadays.

It is interesting to note that the optical rotation for pure (a*R*)-**1** would be −210.25 if calculated from the data for our synthetic sample ([α] −132.46, 63% e.e.) while the value reported for the natural one is −163. If the natural scorodonin indeed has a structure as shown by **1**, it should be a 8.1 : 1 mixture of the two allenic isomers rather than a single enantiomer. Such a phenomenon has been observed with phomallenic acid C and nemotin, which might be common to all similar natural allenic products.[1b,10]

Conclusions

In summary, the structure proposed for the natural allenyne scorodonin was supported by enantioselective synthesis, although two out of seven ^{13}C NMR signals reported in 1980 differ by about 2 ppm each from those of the synthetic sample. The enantiopurity of natural scorodonin was calculated as about 89% or lower; similar values are not uncommon for naturally occurring allenes.

Experimental

General

The ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature using a Varian Mercury 300 or a Bruker Avance 300 instrument. The FTIR spectra were scanned with a Nicolet Avatar 360 FTIR. EIMS and EI-HRMS were recorded with an HP 5989A and a Finnigan MAT 8430 mass spectrometer, respectively. The ESIMS and ESIHRMS were recorded with a PE Mariner API-TOF and an APEX III (7.0 Tesla) FTMS mass spectrometer, respectively. Dry THF was distilled from Na/Ph_2CO under N_2. Unless otherwise specified, all other solvents and reagents were commercially available and used as received without any further purification. PE (chromatography solvent) stands for petroleum ether (60–90 °C).

(3a*R*)-1-(*tert*-Butyldimethylsilyloxy)-7-triethylsilyloxy-hepta-2,3-dien-5-yne (7). *n*-BuLi (ca 2.5 M, in hexanes, 0.8 cm^3, 2.0 mmol) was added to a solution of **4** (357 mg, 2.1 mmol) in anhydrous THF (8 cm^3) stirred at −78 °C under N_2. The mixture was stirred for 30 min. A solution of vacuum/flame-dried $ZnBr_2$ in anhydrous THF (1.0 M, 2.0 cm^3, 2.0 mmol) was introduced. The resulting stock solution (*ca.* 0.18 M) was stirred while the cooling bath was allowed to warm to 0 °C over *ca.* 2 h. A portion of the stock solution of the *in situ* formed zinc reagent (2 cm^3, 0.36 mmol) was then added to another flame-dried flask containing $Pd(PPh_3)_4$ (35 mg, 0.031 mmol) stirred −78 °C under N_2, followed by a solution of bromoallene **6** (160 mg, 0.61 mmol) in dry THF (2 cm^3). The mixture was stirred for 2 h at −78 °C and another 2 h at 0 °C, when TLC showed completion of the reaction. The mixture was partitioned between aqueous sat. NH_4Cl and Et_2O. The phases were separated. The organic layer was washed with brine and dried over anhydrous Na_2SO_4. Removal of the solvent by rotary evaporation and column chromatography (100 : 1 PE/Et_2O) on silica gel gave the allenyne **7** (193 mg, 0.55 mmol, 90%) as a colorless oil: $[\alpha]_D^{26}$ −78.8 (*c* 0.98, $CHCl_3$); 63% e.e. ($t_{R\,(major)}$ = 16.73 min, $t_{R\,(minor)}$ = 19.68 min) as determined by HPLC on a CHIRALPAK OD column (0.46 cm × 25 cm) eluting with *n*-hexane at a flow rate of 0.4 cm^3 min^{-1} with the UV detector set to 220 nm. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.55–5.44 (m, 2H), 4.41 (t, J = 1.3 Hz, 2H), 4.23 (dd, J = 3.3, 5.6 Hz, 2H), 0.98 (t, J = 7.7 Hz, 9H), 0.90 (s, 9 H), 0.65 (q, J = 7.9 Hz, 6H), 0.09 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.7, 94.0, 89.1, 77.4, 76.6, 60.6, 51.80, 25.81, 18.3, 6.7, 4.4, −5.2, −5.3; FTIR (film) 2956, 2930, 2878, 2858, 2737, 2710, 2219, 1951, 1463, 1410, 1363, 1257, 1087 cm^{-1}; EIMS *m*/*z* (%) 351 (M$^+$–1, 0.70), 205 (32), 163 (100), 87 (55), 73 (65); EIHRMS calcd for $C_{19}H_{36}O_2Si_2$ (M$^+$) 352.2254, found 352.2250.

(5a*R*)-7-(*tert*-Butyldimethylsilyloxy)-hepta-4,5-dien-2-yn-1-ol (8). A stock solution of $FeCl_3$ in MeOH (6.2 × 10^{-2} M) was prepared by dissolving $FeCl_3$ (15 mg, 0.093 mmol) in MeOH (1500 cm^3). A portion of this solution (23 cm^3) was added to a flask containing **7** (480 mg, 1.36 mmol). The resulting mixture was stirred at ambient temperature for 2 h before being diluted with EtOAc, washed with water and brine, and dried over anhydrous Na_2SO_4. Removal of the solvent by rotary evaporation and column chromatography (3 : 1 PE/Et_2O) on silica gel gave **8** (264 mg, 1.11 mmol, 81%) as a colorless oil: $[\alpha]_D^{24}$ −116 (*c* 0.93, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.58–5.45 (m, 2H), 4.38 (d, J = 4.4 Hz, 2H), 4.24 (dd, J = 2.9, 5.8 Hz, 2H), 1.70 (t, J = 5.7 Hz, 1H), 0.91 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.8, 94.1, 88.7, 78.1, 76.8, 60.5, 51.4, 25.8, 18.3, −5.26, −5.31; FTIR (film) 3420 (br), 2955, 2929, 2857, 2219, 1951, 1472, 1410, 1257, 1098, 1079, 837, 778 cm^{-1}; EIMS *m*/*z* (%) 237 (M$^+$–1, 0.3), 181 (13), 163 (19), 149 (16), 105 (26), 89 (19), 75 (100); EIHRMS calcd for $C_9H_{13}O_2Si$ (M$^+$–*t*-Bu) 181.0685, found 181.0686.

7-(*tert*-Butyldimethylsilyloxy)-hepta-4,5-dien-2-ynyl chloride (9). 2,6-Lutidine (0.20 cm^3, 1.70mmol) was added to a mixture of anhydrous LiCl (72 mg, 1.70 mmol) in dry DMF (1 cm^3) stirred at 0 °C. The mixture was stirred for 5 min before a solution of **8** (81 mg, 0.34 mmol) was introduced. The stirring was continued at ambient temperature for 2 h. Et_2O was added, followed by aq. sat. NH_4Cl. The phases were separated. The organic layer was washed in turn with aq. sat. $CuSO_4$, water and brine before being dried over anhydrous Na_2SO_4. Removal of the solvent by rotary evaporation and column chromatography (PE) on silica gel gave the chloride **9** (74 mg, 0.29 mmol, 85%) as a colorless oil: $[\alpha]_D^{27}$ −108 (*c* 0.93, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.59–5.45 (m, 2H), 4.27–4.24 (m, 3H), 4.23 (dd, J = 0.9, 2.8 Hz, 1H), 0.91 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.2, 94.5, 84.9, 79.1, 76.6, 60.4, 31.1, 29.7, 18.3, −5.2, −5.3; FTIR (film) 2954, 2928, 2856, 2222, 1951, 1260, 1082, 836, 778 cm^{-1}; EIMS *m*/*z* (%) 199 (M$^+$–*t*-Bu, 14), 165 (28), 123 (67), 93 (100), 89 (70), 73 (83); EIHRMS calcd for $C_9H_{12}OSiCl$ (M$^+$–*t*-Bu) 199.0346, found 199.0351.

(3a*R*)-7-Chloro-hepta-2,3-dien-5-yn-1-ol (1). A mixture of **9** (40 mg, 0.156 mmol) and a THF solution of TBAF (1 M, 0.18 cm^3) was stirred at ambient temperature for 1 h. The mixture was diluted with Et_2O, washed with water and brine, and dried over anhydrous Na_2SO_4. Removal of the solvent by rotary evaporation and column chromatography (2 : 1 PE/Et_2O) on silica gel gave **1** (21 mg, 0.145 mmol, 93%) as an unstable colorless oil with a pungent smell: $[\alpha]_D^{28}$ −132 (*c* 1.00, EtOH). UV (MeOH)$_{\lambda max}$ 223 (sh), 230, 264, 282 nm. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.66 (dtt, J = 6.4, 6.2, 1.1 Hz, 1H), 5.60–5.53 (m, 1H), 4.26 (dd, J = 0.9, 2.4 Hz, 2H), 4.21 (dd, J = 3.0, 6.0 Hz, 2H), 1.79 (br s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.97, 94.41, 85.32, 78.80, 77.35,

59.62, 31.04; FTIR (film) 3327 (br), 2954, 2925, 2854, 2226, 1949, 1463, 1260 cm^{-1}; EIMS *m/z* (%) 144 ($^{37}M^+$, 1.01), 142 ($^{35}M^+$, 3), 114 (4), 112 (12), 107 (73), 79 (46), 77 (100), 51 (38); EIHRMS calcd for C_7H_7OCl $(M)^+$) 142.0185, found 142.0190.

(±)-7-(*tert*-Butyldimethylsilyloxy)-hepta-4,5-dien-2-ynyl acetate (11). A mixture of racemic **8** (112 mg, 0.47 mmol), and DMAP (2 mg, 0.02 mmol) in Ac_2O (0.13 cm^3, 1.40 mmol) was stirred at ambient temperature overnight. The mixture was diluted with Et_2O, washed with water and brine, and dried over anhydrous Na_2SO_4. Removal of the solvent by rotary evaporation and column chromatography (10 : 1 PE/EtOAc) on silica gel afforded acetate **11** (132 mg, 0.47 mmol, 100%) as a colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 5.53 (dtt, $J = 6.4$, 6.4, 1.1 Hz, 1H), 5.50–5.45 (m, 1H), 4.77 (dd, $J = 1.2$, 2.2 Hz, 2H), 4.24 (dd, $J = 1.9$, 2.9 Hz, 1H), 4.22 (dd, $J = 2.4$, 3.0 Hz, 1H), 2.09 (s, 3H), 0.90 (s, 9H), 0.08 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.9, 170.2, 94.4, 84.2, 79.2, 76.5, 60.4, 52.8, 25.8, 20.7, 18.3, −5.24, −5.28; FTIR (film) 2954, 2930, 2885, 2857, 2226, 1952, 1751, 1255, 1222, 1082, 837, 778 cm^{-1}; ESIMS *m/z* 303.0 ($[M+Na]^+$); ESIHRMS calcd for $C_{15}H_{24}O_3SiNa$ ($[M+Na]^+$) 303.13869, found 303.13873.

(±)-7-Hydroxy-hepta-4,5-dien-2-ynyl acetate (12). A mixture of **11** (28 mg, 0.10 mmol) in MeOH–THF (1 : 1 v/v, 1 cm^3) and 6 N HCl (0.1 cm^3) was stirred at ambient temperature for 1 h. The mixture was diluted with Et_2O, washed with water and brine, and dried over anhydrous Na_2SO_4. Removal of the solvent by rotary evaporation and column chromatography (2 : 1 PE/Et_2O) on silica gel afforded alcohol **12** (27 mg, 0.10 mmol, 100%) as a yellowish oil: ^1H NMR (300 MHz, $CDCl_3$) δ 5.63 (q, $J = 6.2$ Hz, 1H), 5.57–5.49 (m, 1H), 4.77 (dd, $J = 1.2$, 2.2 Hz, 2H), 4.24 (dd, $J = 3.1$, 6.0 Hz, 2H), 2.09 (s, 3H), 2.08 (broad, OH, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.9, 170.3, 94.4, 84.6, 78.9, 77.4, 59.7, 52.8, 20.7; FTIR (film) 3410, 2952, 2862, 2256, 1940, 1744, 1266, 1208 cm^{-1}; EIMS *m/z* (%) 166 (M^+, 29), 124 (30), 76 (100); EIHRMS calcd for $C_9H_{10}O_3$ (M^+) 166.0630, found 166.0629.

(±)-7-Chloro-hepta-4,5-dien-2-ynyl acetate (13). 2,6-Lutidine (0.17 cm^3, 1.50 mmol) was added to a mixture of anhydrous LiCl (64 mg, 1.50 mmol) in dry DMF (1 cm^3) stirred at 0 °C. The mixture was stirred for 5 min before a solution of **12** (51 mg, 0.30 mmol) was introduced. The stirring was continued at ambient temperature for 2 h. Et_2O was added, followed by aq. sat. NH_4Cl. The phases were separated. The organic layer was washed in turn with aq. sat. $CuSO_4$, water and brine before being dried over anhydrous Na_2SO_4. Removal of the solvent by rotary evaporation and column chromatography (6 : 1 PE/Et_2O) on silica gel gave the chloride **9** (51 mg, 0.28 mmol, 92%) as a colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 5.74–5.52 (m, 2H), 4.84–4.72 (m, 2H), 4.08 (dd, $J = 2.0$, 6.8 Hz, 2H), 2.10 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.2, 170.2, 91.9, 85.4, 78.1, 77.7, 52.7, 40.8, 20.7; FTIR (film) 2923, 2228, 1952, 1747, 1376, 1223, 1027 cm^{-1}; EIMS *m/z* (%) 184 (M^+, 6), 149 (100), 107 (87), 89 (92), 43 (74); EIHRMS calcd for $C_9H_9O_2Cl$ (M^+) 184.0291, found 184.0294.

(±)-7-Chloro-hepta-4,5-dien-2-yn-1-ol (10). Lipase PS-30 (21 mg) was added to a mixture of **13** (21 mg, 0.11 mmol) in a *p*H 7 (Na_2HPO_4/NaH_2PO_4) buffer and MeCN (8 : 1 v/v, 1 cm^3). The mixture was stirred at ambient temperature for 2 h. The solids were filtered off. The filtrate was diluted with Et_2O, washed with water and brine, and dried over anhydrous Na_2SO_4. Removal of the solvent by rotary evaporation and column chromatography (2 : 1 PE/Et_2O) on silica gel gave the alcohol **10** (14 mg, 0.099 mmol, 92%) as a colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 5.70–5.58 (m, 2H), 4.42–4.34 (m, 2H), 4.08 (dd, $J = 3.0$, 7.0 Hz, 2H), 1.67 (br, 1H, OH); ^{13}C NMR (75 MHz, CD_3COCD_3) δ 213.6, 92.4, 92.2, 78.6, 76.3, 50.9, 41.9; FTIR (film) 3363, 2924, 2856, 2220, 1951, 1717, 1439, 1407, 1248, 1016 cm^{-1}; EIMS *m/z* (%) 144 (^{37}Cl M^+, 4), 142 (^{35}Cl M^+, 12), 107 (31), 77 (100); EIHRMS calcd for C_7H_7OCl $(M)^+$ 142.0185, found 142.0185.

(3a*R*)-Hepta-2,3-dien-5-yne-1,7-diol (8′). Compound **8** (22 mg, 0.092 mmol) was dissolved THF (1 cm^3). A solution of *n*-Bu_4NF (1 M, 0.13 mL, 0.13 mmol) was introduced. The resulting mixture was stirred at ambient temperature for 1 h before being diluted with Et_2O, washed with water and brine, and dried over anhydrous Na_2SO_4. Removal of the solvent by rotary evaporation and column chromatography (1 : 1 PE/Et_2O) on silica gel gave diol **8′** as a colorless oil (9 mg, 0.072 mmol, 79%): $[\alpha]_D^{27}$ −21.0 (*c* 0.33, $CHCl_3$), 64% e.e. ($t_{R\ (major)} = 12.38$ min, $t_{R\ (minor)} = 14.63$ min) as determined by HPLC on a CHFT-IRALPAK AS-H column (0.46 cm × 25 cm) eluting with 80 : 20 n-hexane/*i*-PrOH at a flow rate of 0.7 cm^3 min^{-1} with the UV detector set to 214 nm. ^1H NMR (300 MHz, $CDCl_3$) δ 5.64 (dtt, $J = 6.1$, 5.9, 1.1 Hz, 1H), 5.59–5.54 (m, 1H), 4.39 (dd, $J = 1.0$, 2.1 Hz, 2H), 4.21 (dd, $J = 3.0$, 6.0 Hz, 2H), 1.86 (br, 2H, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.7, 94.2, 89.0, 78.1, 77.7, 59.7, 51.6; FT-IR (film) 3348 (br), 2925, 2854, 2216, 2181, 1949, 1167, 1021, 858 cm^{-1}; EI-MS *m/z* (%) 124 (M^+, 3), 123 (M^+–1, 6), 106 (48), 78 (41), 76 (100), 55 (33), 51 (30); EI-HRMS calcd. for $C_7H_8O_2$ (M^+) 124.0524, found 124.0523.

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