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A New Ring Expansion for a Chiral Hexahydroazulene Skeleton Possessing an Angular Methyl Group

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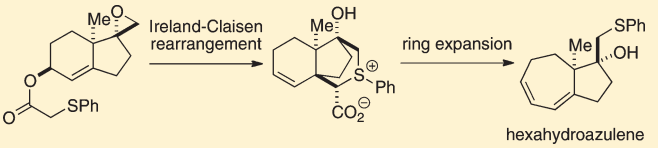
Supporting Information

ABSTRACT: A new synthetic route for a pseudoguaiane ring system is described. The synthesis features an Ireland−Claisen rearrangement for constructing the *trans*-fused ring system, followed by a new ring expansion to yield a bicyclo[5.3.0]decane ring system possessing an angular methyl group.

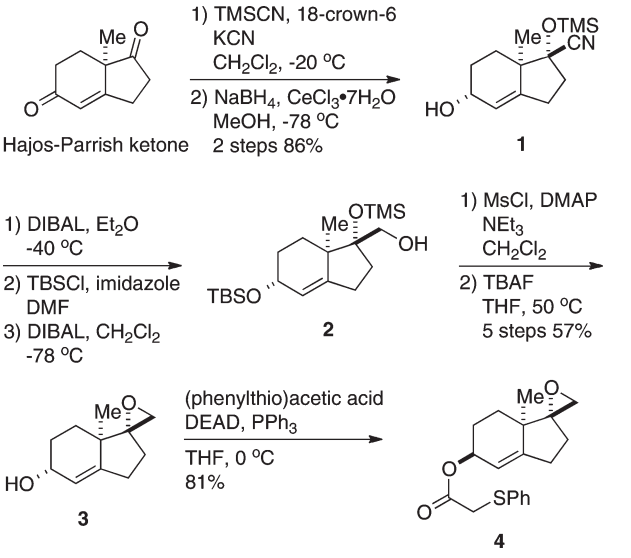


The naturally occurring guaianes and pseudoguaianes are members of a large class of azulenic sesquiterpenes and have been found to exhibit important biological activities.[1−3] These contain a common bicyclo[5.3.0]decane ring system, the skeleton of which differs in the placement of a methyl group. Since the development of an efficient and easily accessible synthetic methodology has been a major issue for synthesis of the 5,7-membered fused ring system of these sesquiterpenes, a variety of synthetic routes have been reported to date.[4−7] We describe herein a new ring expansion that enables to the synthesis of hexahydroazulene possessing a methyl group at the angular position.

In the course of our synthetic studies of solanoeclepin A, the most active hatching agent of potato cyst nematode isolated from hydroponic potato cultures,[8−10] we planned to synthesize the C,D-ring system by an Ireland−Claisen rearrangement of 5-β-thiophenyl acetate prepared from an optically active Hajos−Parrish ketone. The synthesis of 5-β-thiophenyl acetate **4** is illustrated in Scheme 1. Hajos−Parrish ketone[11,12] was treated with TMSCN in the presence of a catalytic amount of 18-crown-6 and KCN,[13] followed by reduction to afford allylic alcohol **1** in 86% yield over two steps. After transformation of the nitrile to aldehyde, protection of the allyl alcohol and subsequent reduction provided alcohol **2**. Mesylation of the alcohol **2** and deprotection of two silyl groups with TBAF gave an intermediate diol, which formed epoxide **3** in 57% yield over five steps. A Mitsunobu reaction employing (phenylthio)acetic acid yielded precursor **4** for the Ireland−Claisen rearrangement.

When the Ireland−Claisen rearrangement[14−16] of **4** was carried out by treatment with an excess amount of KHMDS in the presence of excess TMSCl and pyridine, followed by elevation of the reaction temperature to 60 °C, the product was not the expected **5**, but the zwitterionic compound **6** in 57% yield as a single product (Scheme 2). The structure of **6** was determined by extensive NMR analysis; the newly formed carbon−sulfur bond was undoubtedly determined by HMBC correlation between H-3 and the α-carbon of the carboxylate. The stereochemistry of the ring fusion of **6** was determined by the NOESY correlation of H-5 with H-1 and H-3.

Scheme 1. Synthesis of 5-β-Thiophenyl acetate 4



Surprisingly, the product **6** underwent ring expansion in response to treatment with methanol at 40 °C, giving the cycloheptadiene **7** in 77% yield (Scheme 3). The structure of compound **7** was determined using one- and two-dimensional NMR analyses, with the relative configuration being confirmed by the analysis of NOESY correlations.

The reaction mechanism for the formation of cycloheptadiene **7** is proposed in Scheme 4. The Ireland−Claisen reaction proceeds via (*Z*)-ketene silyl acetal **8** to give a rearrangement product **9**, which would promote cyclization to give the zwitterionic compound **6**. We propose that the formation of cycloheptadiene **7** involves 1,2-migration of the vinylic C−C bond antiperiplanar to

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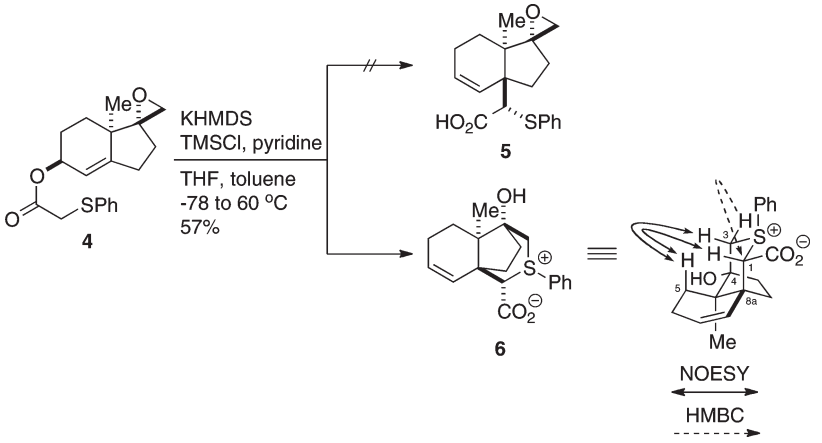
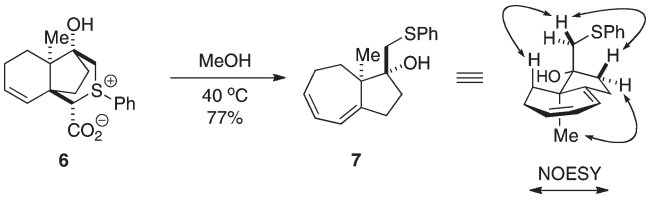
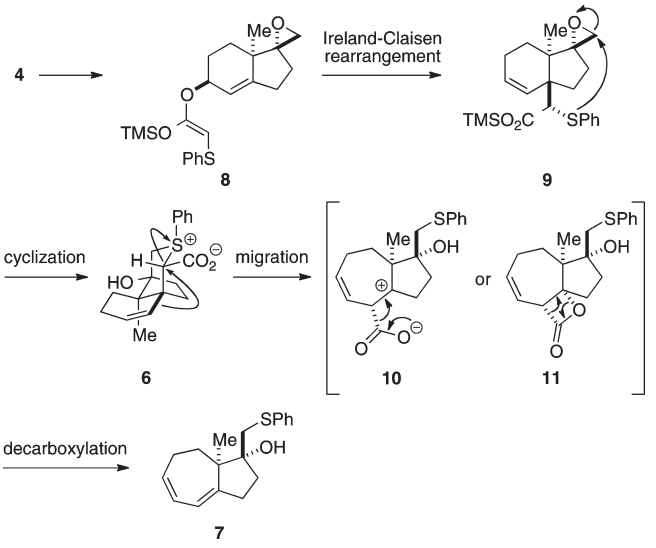
Scheme 2. Ireland−Claisen rearrangement of 4 and Representative NOESY and HMBC Correlations for Zwitterionic Compound 6



Scheme 3. Ring Expansion of Zwitterionic Compound 6 and Representative NOESY Correlation for Cycloheptadiene 7



Scheme 4. Proposed Mechanism for the Formation of Cycloheptadiene 7



the PhS^+ group. In this hypothesis, the chairlike six-membered heterocyclic ring of the zwitterionic compound **6** may be important for the ring expansion as a result of 1,2-migration of the vinylic C−C bond, yielding a zwitterionic intermediate **10** or β-lactone **11**. Finally, decarboxylation[17,18] of **10** or **11** affords the observed product, cycloheptadiene **7**.

In conclusion, the new ring expansion reaction of the Ireland−-Claisen rearrangement product was incidentally discovered. Since the substrate is readily prepared as an optically active form, the reaction should provide a new entry for synthesis of hydroazulenic natural products such as presphaerol,[19] isoreiswigin,[20] and trichoaurantianolide A,[21] including a 5,7-membered fused ring system with a methyl group at the angular position.

EXPERIMENTAL SECTION

(1*R*,5*R*,7a*R*)-5-Hydroxy-7a-methyl-1-((trimethylsilyl)oxy)-2,3,5,6,7,7a-hexahydro-1*H*-indene-1-carbonitrile (1). Hajos−Parrish ketone (4.00 g, 24.4 mmol) and 18-crown-6 (258 mg, 0.976 mmol) were dissolved in CH_2Cl_2 (50 mL) and cooled to −20 °C. To this cold solution were added KCN (318 mg, 4.88 mmol) and trimethylsilyl cyanide (3.40 mL, 26.8 mmol) under nitrogen. After being stirred for 30 min, the reaction mixture was poured into an ice-cooled saturated aqueous $NaHCO_3$ (50 mL). The aqueous layer was separated and extracted with CH_2Cl_2 (30 mL × 3). The extracts were combined, washed with water (50 mL) and brine (50 mL), and then dried over Na_2SO_4. The solution was concentrated to dryness in vacuo. The residue was used for the next reaction without further purification. The residue and $CeCl_3 \cdot 7H_2O$ (11.0 g, 29.3 mmol) were dissolved in MeOH (50 mL), and the mixture was cooled to −78 °C. To this cold solution was added $NaBH_4$ (1.10 g, 29.3 mmol) in one portion under nitrogen. After being stirred for 2 h, the reaction mixture was poured into an ice-cooled mixture of water (40 mL) and EtOAc (40 mL). The mixture was stirred for 2 h, and the aqueous layer was separated and extracted with EtOAc (30 mL × 3). The extracts were combined, washed with water (50 mL) and brine (50 mL), and then dried over Na_2SO_4. The solution was concentrated to dryness in vacuo. The residue was purified by column chromatography (silica gel, hexane/EtOAc 3:2) to give allylic alcohol **1** (5.66 g, 20.9 mmol, 86% in two steps) as a white solid: $[\alpha]^{23}_D$ +90.6 (*c* 1.01, $CHCl_3$); mp 89.5−90.0 °C; IR (KBr) ν_{max} 3315, 2946, 1255, 1156, 845 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.23 (9H, s, $SiMe_3$), 1.06 (3H, br d, J = 1.0 Hz, *Me*), 1.58 (1H, dddd, J = 14.0, 13.0, 9.0, 3.0 Hz, $HOCHCH_AH_B$), 1.70 (1H, dt, J = 13.0, 3.0 Hz, CH_AH_BCMe), 1.90 (1H, td, J = 13.0, 3.0 Hz, CH_AH_BCMe), 2.06 (1H, td, J = 11.5, 6.5 Hz, CH_AH_BCCN), 2.07−2.16 (1H, m, $HOCHCH_AH_B$), 2.29−2.40 (2H, m, CH_AH_BCCN, $CH{=}CCH_AH_B$), 2.56 (1H, tdd, J = 11.5, 5.5, 2.5 Hz, $CH{=}CCH_AH_B$), 4.32−4.39 (1H, m, $HOCHCH{=}C$), 5.50−5.53 (1H, m, $HOCHCH{=}C$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 1.1, 18.2, 24.9, 29.3, 30.6, 35.6, 48.5, 67.9, 81.6, 121.4,

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126.1, 143.8. Anal. Calcd for $C_{14}H_{23}NO_2Si$: C, 63.35; H, 8.73; N, 5.28. Found: C, 63.26; H, 8.67; N, 5.25.

(1*R*,5*R*,7a*R*)-7a-Methyl-2,3,5,6,7,7a-hexahydrospiro[indene-1,2′-oxiran]-5-ol (3). Allylic alcohol **1** (2.00 g, 75.4 mmol) was dissolved in Et_2O (20 mL), and cooled to −78 °C. To this cold solution was added a solution of diisobutylaluminum hydride (1.02 M solution in hexane; 22.4 mL, 22.0 mmol) dropwise. After being stirred for 15 min, the reaction mixture was allowed to warm to −40 °C. After being stirred for 2 h, the reaction mixture was poured into an ice-cooled mixture of water (40 mL) and EtOAc (40 mL). To the mixture was added a saturated aqueous potassium sodium tartrate tetrahydrate (40 mL) solution. The mixture was stirred for 1 h, and the aqueous layer was separated and extracted with EtOAc (30 mL × 2). The extracts were combined, washed with brine (60 mL), and then filtered through a pad of silica gel (10 g) and Na_2SO_4 (10 g). The solution was concentrated to dryness in vacuo. The residue was used for the next reaction without further purification. To a solution of the residue in DMF (15 mL) were added imidazole (1.28 g, 18.9 mmol) and *tert*-butyldimethylsilyl chloride (1.36 g, 9.05 mmol) at room temperature under nitrogen. After being stirred for 30 min, the reaction mixture was poured into a mixture of water (60 mL), hexane (40 mL), and EtOAc (20 mL). The aqueous layer was separated and extracted with a mixture of hexane and EtOAc (2:1, 30 mL × 2). The extracts were combined, washed with water (20 mL) and brine (20 mL), and then dried over Na_2SO_4. The solution was concentrated to dryness in vacuo. The residue was used for the next reaction without further purification. The residue was dissolved in CH_2Cl_2 (40 mL) and cooled to −78 °C. To this cold solution was added a solution of diisobutylaluminum hydride (1.02 M solution in hexane; 7.4 mL, 7.55 mmol) dropwise. After being stirred for 40 min, the reaction mixture was poured into an ice-cooled mixture of water (40 mL) and EtOAc (40 mL). To the mixture was added a saturated aqueous potassium sodium tartrate tetrahydrate (40 mL). The mixture was stirred for 2 h, and the aqueous layer was separated and extracted with EtOAc (30 mL × 3). The extracts were combined, washed with water (30 mL) and brine (30 mL), and then dried over Na_2SO_4. The solution was concentrated to dryness in vacuo. The residue was used for the next reaction without further purification. The residue was dissolved in CH_2Cl_2 (35 mL) and cooled to 0 °C. To this cold solution were added *N*,*N*-dimethyl-4-aminopyridine (1.50 g, 12.0 mmol), triethylamine (4.9 mL, 35.2 mmol), and methanesulfonyl chloride (0.82 mL, 10.6 mmol) under nitrogen. After being stirred at the same temperature for 30 min, the reaction mixture was poured into a mixture of water (60 mL), hexane (30 mL), and EtOAc (30 mL). The aqueous layer was separated and extracted with EtOAc (30 mL × 2). The extracts were combined, washed with water (30 mL) and brine (30 mL), and then filtered through a pad of silica gel (10 g) and Na_2SO_4 (10 g). The solution was concentrated to dryness in vacuo. The residue was used for the next reaction without further purification. To a solution of the residue in THF (35 mL) was added a solution of tetrabutylammonium fluoride (1.0 M solution in THF; 17.6 mL, 17.6 mmol) at room temperature under nitrogen. After being stirred for 10 min, the reaction mixture was heated to 50 °C. After being stirred for 12 h, the reaction mixture was poured into a mixture of water (20 mL) and EtOAc (20 mL). The aqueous layer was separated and extracted with EtOAc (20 mL × 3). The extracts were combined, washed with water (20 mL) and brine (20 mL), and then dried over Na_2SO_4. The solution was concentrated to dryness in vacuo. The residue was purified by column chromatography (silica gel, hexane/EtOAc 1:1) to give epoxide **3** (775 mg, 4.30 mmol, 57% in five steps) as a colorless oil: $[\alpha]^{26}_D$ −30.8 (*c* 1.02 $CHCl_3$); IR (KBr) ν_{max} 3368, 2942, 1457, 1032, 843 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.17 (3H, s, *Me*), 1.34 (1H, td, *J* = 13.0, 3.0 Hz, CH_AH_BCMe), 1.41 (1H, dt, *J* = 13.0, 3.5 Hz, CH_AH_BCMe), 1.59 (1H, tdd, *J* = 13.0, 9.5, 3.5 Hz, $HOCHCH_AH_B$), 1.87 (1H, ddd, *J* = 14.0, 9.5, 7.5 Hz, $MeCCCH_AH_B$), 2.02−2.10 (1H, m, $HOCHCH_AH_B$), 2.10 (1H, ddd, *J* = 14.0, 11.5, 4.5 Hz, $CH{=}CCH_AH_B$), 2.25 (1H, dddt, *J* = 14.0, 9.5, 4.5, 1.0 Hz, $MeCCCH_AH_B$), 2.56−2.65 (1H, m, $CH{=}CCH_AH_B$), 2.66 (1H, d, *J* = 4.5 Hz, $MeCC(O)CH_AH_B$), 2.92 (1H, d, *J* = 4.5 Hz, $MeCC(O)CH_AH_B$), 4.24−4.32 (1H, m, $HOCHCH{=}C$), 5.42−5.45 (1H, m, $HOCHCH{=}C$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 27.0, 29.1, 29.6, 31.2, 40.4, 53.7, 68.2, 70.0, 122.1, 149.5. Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.13; H, 8.92.

(1*R*,5*S*,7a*R*)-7a-Methyl-2,3,5,6,7,7a-hexahydrospiro[indene-1,2′-oxiran]-5-yl 2-(Phenylthio)acetate (4). Epoxide **3** (450 mg, 2.50 mmol) and triphenylphosphine (1.05 g, 4.00 mmol) were dissolved in THF (25 mL), and the mixture ws cooled to 0 °C. To the cold solution were added (phenylthio)acetic acid (0.75 g, 3.75 mmol) and a solution of diethyl azodicarboxylate (2.2 M solution in toluene; 1.8 mL, 4.00 mmol). After being stirred at the same temperature for 40 min, the reaction mixture was concentrated to dryness in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc 9:1) to give 5-*β*-thiophenyl acetate **4** (662 mg, 2.00 mmol, 80%) as a colorless oil: $[\alpha]^{27}_D$ −177.0 (*c* 0.99 $CHCl_3$); IR (KBr) ν_{max} 1727, 1271, 1122, 742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.06 (3H, s, *Me*), 1.20 (1H, dt, *J* = 13.0, 4.0 Hz, CH_AH_BCMe), 1.27 (1H, td, *J* = 13.0, 3.5 Hz, CH_AH_BCMe), 1.69 (1H, dddd, *J* = 15.0, 4.5, 3.0, 1.0 Hz, $CH_AH_BCH_2CMe$), 1.80−1.87 (1H, m, $CH_AH_BCH_2CMe$), 1.88 (1H, ddd, *J* = 14.0, 9.5, 7.0 Hz, $MeCCCH_AH_B$), 2.11 (1H, ddd, *J* = 14.0, 12.0, 5.0 Hz, $MeCCCH_AH_B$), 2.30 (1H, ddd, *J* = 16.0, 9.5, 5.0 Hz, $CH{=}CCH_AH_B$), 2.63 (1H, dddt, *J* = 16.0, 12.0, 7.0, 2.5 Hz, $CH{=}CCH_AH_B$), 2.67 (1H, d, *J* = 5.0 Hz, $MeCC(O)CH_AH_B$), 2.94 (1H, d, *J* = 5.0 Hz, $MeCC(O)CH_AH_B$), 3.59 (1H, d, *J* = 15.0 Hz, $(O{=})CCH_AH_BSPh$), 3.63 (1H, d, *J* = 15.0 Hz, $(O{=})CCH_AH_BSPh$), 5.18−5.24 (1H, m, $(O{=})COCHCH{=}C$), 5.41−5.45 (1H, m, $(O{=})COCHCH{=}C$), 7.19−7.24 (1H, m, aromatic), 7.25−7.31 (2H, m, aromatic), 7.38−7.42 (2H, m, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.7, 24.8, 26.8, 27.2, 29.0, 36.8, 40.2, 53.7, 68.1, 70.0, 115.7, 126.9, 128.9, 130.0, 135.0, 153.2, 169.3. Anal. Calcd for $C_{19}H_{22}O_3S$: C, 69.06; H, 6.71. Found: C, 68.89; H, 6.60.

(4*R*,4a*R*,8a*S*)-4-Hydroxy-4a-methyl-2-phenyl-2,3,4,4a,5,6-hexahydro-1*H*-4,8a-ethanoisothiochromen-2-ium 1-Carboxylate (6). 5-*β*-Thiophenyl acetate **4** (520 mg, 1.57 mmol) was dissolved in THF (30 mL), and cooled to −78 °C. To this cold solution were added freshly distilled chlorotrimethylsilane (5.90 mL, 46.8 mmol) and pyridine (3.80 mL, 47.2 mmol) followed by a solution of potassium bis(trimethylsilyl)amide (0.5 M solution in toluene; 63.0 mL, 3.14 mmol). After being stirred for 30 min at the same temperature, the reaction mixture was allowed to warm to ambient temperature and then heated to 60 °C. After being stirred for 4 h, the reaction mixture was poured into water (20 mL). The organic layer was separated and extracted with water (10 mL × 3). The aqueous layers were combined and concentrated to dryness in vacuo. The residue was purified by reversed-phase chromatography (Cosmosil 75C_{18}-OPN, 5% CH_3CN/H_2O) to give zwitterionic compound **6** (298 mg, 0.902 mmol, 57%) as a white powder: $[\alpha]^{26}_D$ +56.4 (*c* 0.20 H_2O); mp 132.0−133.0 °C; IR (KBr) ν_{max} 3387, 1629, 1339, 749 cm^{-1}; ^1H NMR (600 MHz, CD_3OD) δ 1.18 (3H, s, *Me*), 1.69 (1H, br dd, *J* = 14.0, 8.0 Hz, H-5), 1.95 (1H, dddd, *J* = 14.0, 12.0, 6.5, 2.0 Hz, H-9), 2.20 (1H, dt, *J* = 14.0, 8.0 Hz, H-5′), 2.24−2.36 (3H, m, H-6, H-10, H-10′), 2.44−2.53 (1H, m, H-6′), 2.52 (1H, ddd, *J* = 13.5, 8.0, 5.5 Hz, H-9′), 3.62 (1H, d, *J* = 12.0 Hz, H-3), 3.87 (1H, d, *J* = 12.0 Hz, H-3′), 4.32 (1H, s, H-1), 5.73 (1H, dt, *J* = 9.5, 3.0 Hz, H-7), 5.78 (1H, br d, *J* = 9.5 Hz, H-8), 7.70 (2H, br t, *J* = 7.5 Hz, aromatic), 7.78 (1H, br t, *J* = 7.0 Hz, aromatic), 8.01 (2H, br d, *J* = 7.0 Hz, aromatic); ^{13}C NMR (150 MHz, CD_3OD) δ 17.5, 23.7, 24.3, 27.1, 36.4, 44.2, 48.3, 51.9, 69.3, 79.4, 125.3, 130.1, 130.6, 131.9, 132.2, 135.4, 168.2. Anal. Calcd for $C_{19}H_{22}O_3S$: C, 69.06; H, 6.71. Found: C, 69.05; H, 6.68.

(1*R*,8a*R*)-8a-Methyl-1-((phenylthio)methyl)-1,2,3,7,8,8a-hexahydroazulen-1-ol (7). Zwitterionic compound **6** (200 mg, 0.605 mmol) was dissolved in MeOH (6 mL) and heated to 40 °C under nitrogen. After being stirred for 112 h, the reaction mixture was concentrated to dryness in vacuo. The residue was purified by column chromatography (silica gel, hexane/EtOAc 1:9) to give cycloheptadiene **7** (133 mg, 0.464 mmol, 77%) as a colorless oil. $[\alpha]^{25}_D$ +101.4 (*c* 1.03

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$CHCl_3$); IR (KBr) ν_{max} 3465, 2926, 1718, 1583, 1481, 1439, 1027 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 1.15 (3H, s, *Me*), 1.44 (1H, td, *J* = 12.0, 5.0 Hz, CH_AH_BCMe), 1.64 (1H, dt, *J* = 12.0, 3.5 Hz, CH_AH_BCMe), 1.90−2.04 (1H, m, $HOCCH_AH_B$), 2.11−2.24 (2H, m, $HOCCH_AH_B$, $CH{=}CCH_AH_B$), 2.29−2.42 (3H, m, $CH{=}CCH_AH_B$, $CH_2CH{=}CH$), 3.02 (1H, d, *J* = 13.0 Hz, CH_AH_BSPh), 3.16 (1H, dd, *J* = 13.0, 2.0 Hz, CH_AH_BSPh), 5.63 (1H, br d, *J* = 7.5 Hz, $CH{=}CHCH{=}C$), 5.75 (1H, ddd, *J* = 12.0, 5.5, 3.0 Hz, $CH{=}CHCH{=}C$), 5.90 (1H, ddd, *J* = 12.0, 7.5, 2.5 Hz, $CH{=}CHCH{=}C$), 7.00−7.06 (1H, m, aromatic), 7.08−7.14 (2H, m, aromatic), 7.41−7.46 (2H, m, aromatic); ^{13}C NMR (100 MHz, C_6D_6) δ 19.3, 27.5, 28.4, 28.6, 33.9, 42.8, 51.7, 83.5, 118.3, 123.9, 126.3, 129.2, 130.0, 131.4, 138.0, 152.2. Anal. Calcd for $C_{18}H_{22}OS$: C, 75.48; H, 7.74. Found: C, 75.48; H, 7.70.

■ ASSOCIATED CONTENT

Supporting Information. Copies of ^1H NMR and ^{13}C NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

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■ REFERENCES

(1) Zhan, Z.-J.; Ying, Y.-M.; Ma, L.-F.; Shan, W.-G. *Nat. Prod. Rep.* **2011**, *28*, 594–629.
(2) Fraga, B. M. *Nat. Prod. Rep.* **2010**, *27*, 1681–1708.
(3) Fraga, B. M. *Nat. Prod. Rep.* **2007**, *24*, 1350–1381.
(4) Heathcock, C. H.; Graham, S. L.; Pirrung, M. C.; Plavac, F.; White, C. T. In *The Total Synthesis of Natural Products*; ApSimon, J., Ed.; Wiley: New York, 1983; Vol. 5.
(5) Pirrung, M. C.; Morehead, A. T., Jr.; Ypung, B. C. In *The Total Synthesis of Natural Products*; Goldsmith, D., Ed.; Wiley: New York, 2000; Vol. 11.
(6) Hudlichy, T.; Reed, J. W. In *The Way of Synthesis*; Wiley-VCH: Weinheim, 2007, pp 277−340.
(7) Foly, D. A.; Maguire, A. R. *Tetrahedron* **2010**, *66*, 1131–1175.
(8) Mulder, J. G.; Diepenhorst, P.; Brüggemann-Rotgans, I. E. M. PCT Int. Appl. WO 93/02,083; *Chem. Abstr.* **1993**, *118*, 185844z.
(9) Schenk, H.; Driessen, R. A. J.; de Gelder, R.; Goubitz, K.; Nieboer, H.; Brüggemann-Rotgans, I. E. M.; Diepenhorts, P. *Croat. Chem. Acta* **1999**, *72*, 593–606.
(10) Recently, the first total synthesis of solanoeclepin A was reported by Tanino and Miyashita; see: Tanino, K.; Takahashi, M.; Tomata, Y.; Tokura, H.; Uehara, T.; Narabu, T.; Miyashita, M. *Nat. Chem.* **2011**, *3*, 484–488.
(11) Hajos, Z. G.; Parrish, D. R. *J. Org. Chem.* **1974**, *39*, 1615–1621.
(12) Hajos, Z. G.; Parrish, D. R. *Organic Synthesis*; Wiley: New York, 1990; Collect. Vol. VII, pp 363−368.
(13) Evans, D. A.; Truesdale, L. K. *Tetrahedron Lett.* **1973**, *49*, 4929–4932.
(14) Ireland, R. E.; Mueller, R. H. *J. Am. Chem. Soc.* **1972**, *94*, 5897–5898.
(15) Richardson, S. K.; Sabol, M. R.; Watt, D. S. *Synth. Commun.* **1989**, *19*, 359–367.
(16) Castro, A. M. M. *Chem. Rev.* **2004**, *104*, 2939–3002.
(17) Mulzer, J.; Zippel, M.; Bruntrup, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 465–466.
(18) Mulzer, J.; Zippel, M. *Tetrahedron Lett.* **1980**, *21*, 751–754.
(19) Cafieri, F.; Fattorusso, E.; Blasio, B. D.; Pedone, C. *Tetrahedron Lett.* **1981**, *22*, 4123–4126.
(20) Kashman, Y.; Hirsch, S. *J. Nat. Prod.* **1991**, *54*, 1430–1432.
(21) Invernizzi, A. G.; Vidari, G.; Vita-Finzi, P. *Tetrahedron Lett.* **1995**, *36*, 1905–1908.